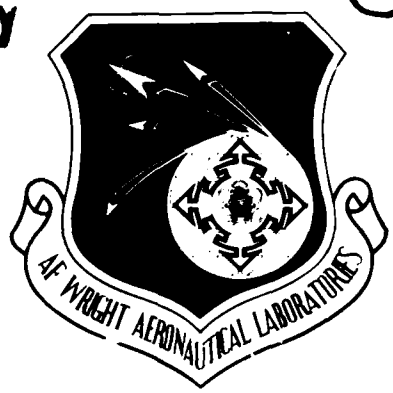
(2)



AFWAL-TR-87-2042
Volume II

PRODUCTION OF JET FUELS FROM COAL-DERIVED LIQUIDS

VOL II - Characterization of Liquid By-Products from the Great Plains Gasification Plant

C. L. KNUDSON

UNIVERSITY OF NORTH DAKOTA
ENERGY AND MINERAL RESEARCH CENTER
GRAND FORKS ND 58202

MAY 1988

INTERIM REPORT FOR THE PERIOD 26 NOVEMBER 1986 - 1 FEBRUARY 1988

AERO PROPULSION LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433-6563

NOTICE

When Government drawings, specifications, or other data are used for any other purpose other than in connection with a definitely Government-related procurement, the United States Government incurs no responsibility or any obligation whatsoever. The fact that the Government may have formulated or in any way supplied the said drawings, specifications, or otherwise in any manner construed, as licensing the holder, or any other person or corporation; or as conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This report has been reviewed by the Office of Public Affairs (ASD/PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

William E. Harrison III

WILLIAM E. HARRISON III
Fuels Branch
Fuels and Lubrication Division
Aero Propulsion Laboratory

Charles L Delaney

CHARLES L. DELANEY, Chief
Fuels Branch
Fuels and Lubrication Division
Aero Propulsion Laboratory

FOR THE COMMANDER

Robert D. Sherrill

ROBERT D. SHERRILL, Chief
Fuels and Lubrication Division
Aero Propulsion Laboratory

"If your address has changed, if you wish to be removed from our mailing list, or if the addressee is not longer employed by your organization, please notify AFWAL/POSF, Wright-Patterson AFB, Ohio 45433-6563 to help us maintain a current mailing list."

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION: Unclassified	1b. RESTRICTIVE MARKINGS: None
2a. SECURITY CLASSIFICATION AUTHORITY: N/A	3. DISTRIBUTION/AVAILABILITY OF REPORT: Approved for public release; distribution unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE: N/A	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S): AFWAL-TR-87-2042, Vol II
6a. NAME OF PERFORMING ORGANIZATION: University of North Dakota Energy & Minerals Research Ctr; 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION: Air Force Wright Aeronautical Laboratories Aero Propulsion Laboratory (AFWAL/POSF)
6c. ADDRESS (City, State, and ZIP Code): Box 8213, University Station Grand Forks, ND 58202	7b. ADDRESS (City, State, and ZIP Code): Wright-Patterson Air Force Base, Ohio 45433-6563
8a. NAME OF FUNDING/SPONSORING ORGANIZATION: Air Force Wright Aeronautical Laboratories; 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: FY1455-86-N0657
8c. ADDRESS (City, State, and ZIP Code): AFWAL/POSF Wright -Patterson AFB OH 45433-6563	10. SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO. 63215F; PROJECT NO. 2480; TASK NO 16; WORK UNIT ACCESSION NO. 01

11. TITLE (Include Security Classification)
Production of Jet Fuels from Coal Derived Liquids, Vol II
Characterization of Liquid By-Products from the Great Plains Gasification Plant

12. PERSONAL AUTHOR(S)
C.L. Knudson

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Interim	FROM 861126 TO 880201	May 1988	120

16. SUPPLEMENTARY NOTATION
Cont'd from pg. 1

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	
21	21	07	Jet Fuel, Turbine Fuel, JP-4, JP-8, Crude Phenol, Tar Oil, Naphtha, Great Plains Gasification Plant, Chemical Analysis, JFTS
04	05	03	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

In September 1986, the Fuels Branch of the Aero Propulsion Laboratory at Wright-Patterson Air Force Base, Ohio, commenced an investigation of the potential of the production of jet fuel from the liquid by-product streams produced by the gasification of lignite at the Great Plains Gasification Plant in Beulah, North Dakota. Funding was provided to the Department of Energy (DOE) Pittsburgh Energy Technology Center (PETC) to administer the experimental portion of this effort. This report details the program with the University of North Dakota Energy and Mineral Research Center to determine the chemical and physical properties of the by-product liquid streams and assess their suitability for the production of jet fuel.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT: ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION: UNCLASSIFIED
22a. NAME OF RESPONSIBLE INDIVIDUAL: William E. Harrison III	22b. TELEPHONE (Include Area Code): (513) 255-6601; 22c. OFFICE SYMBOL: AFWAL/POSF

DD Form 1473, JUN 86 *Previous editions are obsolete.*

SECURITY CLASSIFICATION OF THIS PAGE

UNCLASSIFIED

DISCLAIMER

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, mark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of the authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

FOREWORD

In September 1986, the Fuels Branch of the Aero Propulsion Laboratory at Wright-Patterson Air Force Base, Ohio commenced an investigation of the potential for production of jet fuel from the liquid by-product streams produced by the gasification of lignite at the Great Plains Gasification Plant in Beulah, North Dakota. Funding was provided to the Department of Energy (DOE) Pittsburgh Energy Technology Center (PETC) to administer the experimental portion of this effort. This report details the effort of the University of North Dakota Energy and Mineral Research Center (UNDEMRC), who, as a contractor of DOE (DOE Contract No. DE-AC22-87PC90016), characterized these liquid by-product streams. DOE/PETC was funded through Military Interdepartmental Purchase Request (MIPR) FY1455-86-N0657. Mr William E. Harrison III was the Air Force project engineer, Mr Gary Stiegel was the DOE/PETC project engineer, and Dr Warrack Willson was the UNDEMRC project manager.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (cont.)

LIST OF TABLES

EXECUTIVE SUMMARY

The Great Plains Gasification Plant (GPGP) represents the first commercial Syn-Fuels Plant in the United States. The Plant is being operated for the Department of Energy by the ANG Coal Gasification Company to produce 150 MM SCF of synthetic natural gas (SNG) per day. During its continued operation, significant process improvements have been made, and potentially this study will lead to more improvements. The GPGP produces three by-product hydrocarbon liquid streams (rectisol naphtha, crude phenol and tar oil) which are utilized as plant fuel. The purpose of this work was to characterize these streams in order to more fully understand what would be necessary to produce jet fuel or other more valuable products from these streams. Potential product slates have been addressed in AFWAL-TR-87-2042, Vol. I, "Market Assessment for Liquid By-Products from the Great Plains Gasification Plant", J.E. Sinor, August, 1987.

The rectisol naphtha is mostly benzene-toluene-xylene (BTX) material. In the raw form it has a strong odor which can be reduced by sweetening and contains very volatile components including acetone and pentadienes. The major upgraded product would be expected to be benzene, where the value could range from $1.00-1.20/gal as a chemical feedstock.

The crude phenol stream contains high concentrations of phenol and lesser amounts of cresols. Higher boiling dihydroxybenzenes are present. The major product recovered from this stream is phenol, which might be valued as high as $2.00/gal.

The tar oil stream is composed of four major compound types: neutral aromatics, phenolic aromatics, nitrogen containing aromatics, and straight chain aliphatics. This stream can be processed to produce specification jet fuel, but at high hydrogen consumption levels due to high aromaticity and the presence of hetero-atoms. It is highly aromatic, and the resulting jet fuel (from lower level hydrotreating) would be expected to have a higher density and be a candidate for a new class of jet fuels. The actual quantity of the stream is small compared to petroleum industry standards, and the quantity of fuel produced would be small. However, it would be a United States produced fuel, and usable at Northern Tier Air Force bases.

The production of usable fuels and products from liquid by-product streams would aid the GPGP and improve the design and economics of future gasification plants. In fact without improved economics, no additional gasification plants will be constructed in the United States.

GOALS AND OBJECTIVES

The goal of the national energy policy is to foster an adequate supply of energy at a reasonable cost. Domestic production in the United States supplies approximately 60% of the petroleum requirements. However, domestic and world supplies have been and will continue to be unreliable in the future. Continued dependence upon foreign suppliers of crude oil could seriously affect our nation's economy as well as jeopardize our national security. As such, synthetic liquid fuels are an essential part of an energy scenario which provides the United States with a means to reduce reliance on imported oil.

The Department of Defense (DOD) is the largest single consumer of liquid fuels in the United States, accounting for 2.7% of the nation's petroleum demand. Approximately one-half of the DOD requirements of Grade JP-4 turbine fuel, or 240,000 barrels, are consumed daily by the Air Force for aircraft operations. JP-4 is a naphtha -based fuel used primarily in the United States, while JP-8 is a kerosene-type fuel which is used abroad. Because of the need to assure adequate supplies of both types of turbine fuel at acceptable costs, the Air Force has investigated the characteristics, cost, and yield of these fuels when produced from tar sands, shale oil, and heavy oils, and is seeking similar data for coal-derived liquids.

The Great Plains Gasification Plant (GPGP) in Beulah, North Dakota, is in close proximity to several Air Force bases along our northern tier. This plant is producing 150 million cubic feet per day of high-Btu synthetic natural gas (SNG) from North Dakota lignite. In addition, the plant generates three liquid by-product streams: rectisol naphtha, crude phenol, and tar oil. The naphtha, about 880 barrels per day (BPD), may be directly marketable because of its low boiling point and high aromatic content. The nominal 920 BPD of phenols from the Phenosolvan unit may be marketed, after processing, as valuable phenol and/or benzene. The 3450 BPD of tar oil from the primary quench, is available as potential source of aviation jet fuel for the Air Force. Aviation fuels produced from the GPGP tar oil could become an indigenous fuel supply for the northern tier bases. The Air Force base at Minot, North Dakota, is remote from jet fuel supplies and would especially benefit from this development if the jet fuel produced at Great Plains can meet all specifications and is cost competitive.

The primary objective of this project is to assess the technical and economic feasibility of producing aviation turbine

fuel from the by-product streams of GPGP. These streams, as well as fractions thereof, will be characterized and subsequently processed over a wide range of process conditions. The chemical and physical characteristics of the resulting turbine fuel products will be compared to petroleum-based fuels to determine their ability to meet military specification requirements. This interim report covers the characterization of the three GPGP by-product streams.

FEEDSTOCK ASSESSMENT

Stream Assessment

The quantity of the liquid by-products produced at the GPGP is primarily a function of the amount of coal gasified (or SNG produced) and operating conditions and, to a much lesser extent, of the coal feed. This latter effect stems from the fact that the Beulah-Zap lignite mined for use at the GPGP actually consists of four laterally continuous lithologic layers (1). Preliminary investigations at UNDEMRC have shown that the constituents of these distinct layers have different properties, including friability, Btu values, gas/tar yields, and ash chemistry (2). However, since no attempt is made at the mine to segregate layers, but rather the entire seam is mined continuously, these variations will be averaged during normal operation.

Nameplate plant capacity is 137 MM SCF of SNG per day from 14,000 TPD of Beulah-Zap lignite. Recently the output of gas has been increased to 150 MM SCF per day from 16,000 TPD of lignite. The effect of the increased rate and any further increases will increase the amount of by-products proportionally, and their effect on the by-product quality will be presumed to be minimal.

For JP-4 or JP-8 production the preferred feed is the mid 60%-70% (2100-2400 Bbl/D) of the tar oil (430°-600°F distillation cut) and the bottom nominal 30% (280 Bbl/D) of the crude phenols (+430°F fraction). The distillation would remove the phenolics which would form naphtha-range material upon hydrogenation which is too light for jet fuels. The distillates would have more value for their phenol content. Rejection of the tar oil bottoms would remove solids, reduce the nitrogen content, and remove low hydrogen content materials from the resulting feedstock. The addition to the feedstock of the phenolic bottoms is less preferred and is only to provide additional feedstock since they are relatively high in oxygen and nitrogen.

Feedstock Characterization

In order to evaluate potential uses of the GPGP liquid by-product streams, feedstock characterization work has been performed. The samples being analyzed include the rectisol naphtha, crude phenol, and tar oil streams as well as various distillation cuts and compound-type fractions. Distillation cuts from ASTM D86 distillations for both the crude phenol and tar oil streams have been analyzed. Elemental and component analyses have been performed on true boiling point distillation cuts of the crude phenol stream. Compound-type fractions (aliphatics, aromatics, and polars) have been prepared and analyzed as well as acid, neutral, and base fractions. Instruments being used include GC, GC/MS, and NMR. This section summarizes the data and relates it to aviation fuel. The following sections present information on the experimental techniques used and data for each by-product stream.

The volatility of the three by-product streams and an aviation jet fuel (AV Jet A) are depicted in Figure 1 and tabulated in Table 1. The rectisol naphtha stream is very volatile and only a small amount is in the volatility range of a jet fuel. The light ends of the rectisol naphtha stream (components with boiling points below benzene) include oxygenated compounds such as acetone and butanone, numerous pentadienes which are potential gum formers, and volatile thiols (methanethiol and ethanethiol) which give it an unbearable odor. These light ends constitute 16 area% of the GC spectra which would be over 20 wt% of the rectisol naphtha stream. The difficulty of calculating wt% data from GC area% data is discussed in the experimental section. The major components in this stream are benzene (46.6 area%) and toluene (17.6 area%), or approximately 40 wt% and 14 wt%, respectively. Figure 2 depicts the cumulative area% values for compounds eluting from a gas chromatograph versus the boiling point of the particular compound for the three streams. The large concentrations of benzene and toluene are readily apparent. The individual amounts of the other compounds are small.

The crude phenol indicates a distillation distribution that overlaps that of aviation fuel. However, this is misleading and shows why compound-type analysis or component data are required to evaluate coal-derived feedstocks. The main components of the phenol stream are phenol and the cresols. Hydrogenation would produce low-boiling cyclohexane and methylcyclohexane while consuming a lot of hydrogen gas.

Table 2 presents data for the amount of aliphatics, aromatics and polar fractions for the crude phenol and tar oil streams and for the aviation fuel. As illustrated in Table 2, the crude phenol stream contains 92 wt% of polars and under 3 wt% of

aromatics and aliphatics. Figure 2 indicates the presence of three major compounds: phenol and the cresols. The proton NMR spectrum (Figure 3) and data (Table 3) verify that this stream is essentially phenolic. The strong single-ring-aromatic proton resonance peaks around 7 ppm, the phenolic-hydroxyl proton peak between 4 and 5 ppm, and the alkyl-methyl proton peaks at 2.2 ppm as well as the near absence of aliphatic-methyl peaks at 0.9 ppm indicate the phenolic nature of this stream. GC component data of the total stream and data for the true boiling point distillation fractions indicate that (excluding water) the initial 60 wt% of this stream is mainly phenol and cresol while the bottom 33 wt% contains numerous dimethylphenols and dihydroxybenzene compounds. Elemental analysis of ASTM D86 distillation fractions indicates oxygen contents of 16 to 19 wt% in the bottom 30 wt%. Hydrogenation of the heavy ends would produce methyl- and dimethylcyclohexane and consume even more hydrogen to produce water due to the presence of dihydroxybenzenes. Hydrogenation of the crude phenol stream would, therefore, consume a lot of hydrogen to produce very light material.

The volatility of the tar oil stream also overlaps that of aviation fuel (Figure 1) and JP-4 and JP-8 (Figure 4). About 36 wt% of the stream is polars (Table 2) and at least 3 wt% is nitrogen bases. Much of the polars are phenolic and therefore extractable by base. The nitrogen bases include quinoline and can be extracted by hydrochloric acid. The main components are methylated one- and two-ring aromatics. The aromatic and phenolic nature of the tar oil stream is also indicated by the hydrogen content of about 9 wt% and oxygen content of almost 7 wt%. During hydrogenation of this stream the phenolics would react to light material while the two-ring aromatics would form methylated-decalin material. The presence of nitrogen bases as well as residual insolubles would have to be addressed.

Of the three liquid by-product streams, the tar oil stream is the most appropriate to be used to produce jet fuel. The rectisol naphtha stream after removal of the light ends would be high in BTX. The crude phenol stream would provide mainly phenol since guaiacol and dihydroxybenzenes may contaminate the cresols. However, this stream is being tested in the Dynaphen Process by Hydrocarbon Research, Inc. (HRI) which may be able to refine crude phenols into benzene and phenol.

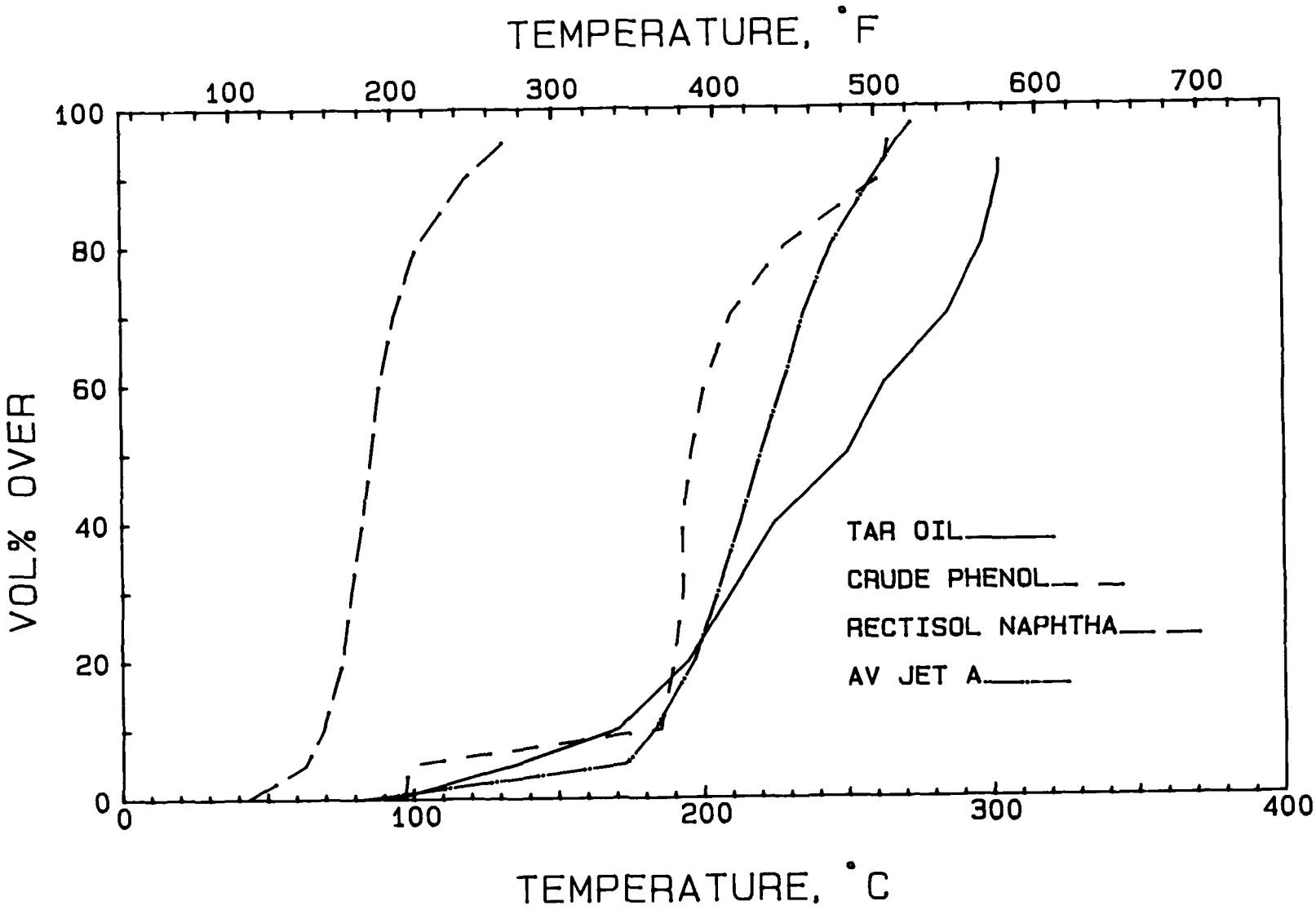


Figure 1. D86 distillation profiles of tar oil, crude phenol, rectisol naphtha, and AV Jet A.

TABLE 1

ASTM D86 DISTILLATION DATA

	Tar Oil	Crude Phenol	Rectisol Naphtha	AV Jet A
Barr. Press. (mm Hg)	756	742	731	742
Rm. Temp., °C (°F)	23(73)	23(73)	24(75)	23(73)
Vol. % Distil.:				
IBP	93(199)	97(206)	43(109)	82(179)
5%	135(275)	98(208)	63(145)	173(343)
10%	170(338)	185(365)	69(156)	183(361)
20%	195(383)	190(374)	76(168)	197(386)
30%	210(410)	193(379)	79(174)	205(401)
40%	225(437)	193(379)	83(181)	213(415)
50%	250(482)	196(384)	86(186)	220(428)
60%	263(505)	201(393)	89(192)	228(442)
70%	285(545)	210(410)	94(201)	235(455)
80%	297(566)	229(444)	102(215)	245(473)
90%	303(577)	263(505)	119(246)	260(500)
95%			132(269)	268(514)
Max. Temp., °C (°F)	303(577)	265(509)	132(269)	274(525)
Max. Vol., %	92	95	96	98
Residue wt%	9.66	5.75	2.80	2.20
Recovery wt%	87.68	92.45	96.35	96.21
Lost wt%	2.66	1.80	0.85	1.59
Sp. Gr.	1.015	1.060	0.821	0.817
	Elemental Analysis, wt% AR			
Carbon	83.76	72.18	87.65	87.68
Hydrogen	8.83	7.49	10.12	14.30
Nitrogen	0.52	0.28	0.00	0.06
Sulfur	0.39	0.04	0.00	0.17
KF-water[a]	1.20	4.48		0.01
THFI[b]	0.11	0.00		

[a] Water determined by Karl Fisher titration.
[b] Tetrahydrofuran insolubles (0.5 micron filter).

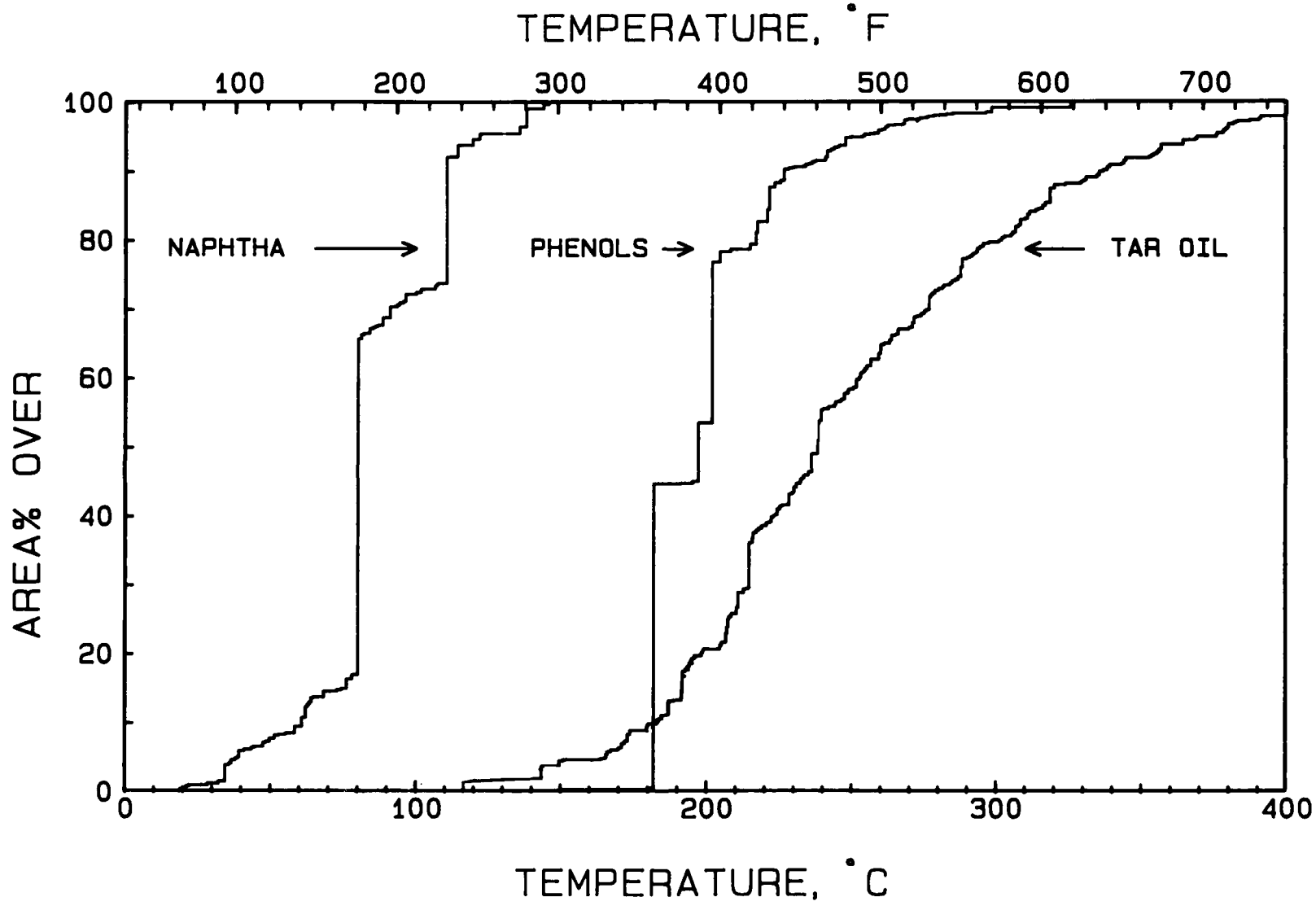


Figure 2. Cumulative GC area% profiles of tar oil, crude phenol, and rectisol naphtha.

TABLE 2

ELEMENTAL ANALYSES OF TOTAL AND COLUMN FRACTIONS

	Fraction wt%	C	H	N	S	O&S	KF-water[a]
Crude Phenols							
Total	100.0	72.18	7.49	0.28	0.04	20.05	4.48
Aliphatics[b]	0.5						
Aromatics	1.8	81.41	7.50	0.29	NA[c]	10.80	----
Polars	92.5	73.62	7.32	0.32	NA	18.74	----
Recovery	94.8						
Tar Oil							
Total	100.0	83.76	8.83	0.52	0.39	6.89	1.20
Aliphatics	7.9	86.60	14.89	0.11	NA	-1.60	
Aromatics	47.7	88.82	8.36	0.20	NA	2.62	
Polars	35.7	75.46	7.62	0.85	NA	16.07	
Recovery	91.3						
AV Jet-A							
Total 1)	100.0	87.12	14.19	0.17	----	-1.48	
2)		87.68	14.30	0.06	0.17		
Aliphatics	76.7	86.33	15.03	0.33	NA	-1.69	
Aromatics	18.4	88.99	10.67	0.21	NA	0.13	
Polars[b]	1.9						
Recovery	97.0						
Standards							
Tetralin		90.46	9.28	0.24		0.02	
$C_{10}H_{12}$ Theory		90.91	9.04	0			
Cyclohexane		86.53	14.97	0.29		-1.79	
C_6H_{12} Theory		85.71	14.28	0			

[a] Karl-Fisher analysis.
[b] Sample too small.
[c] NA indicates not analyzed.

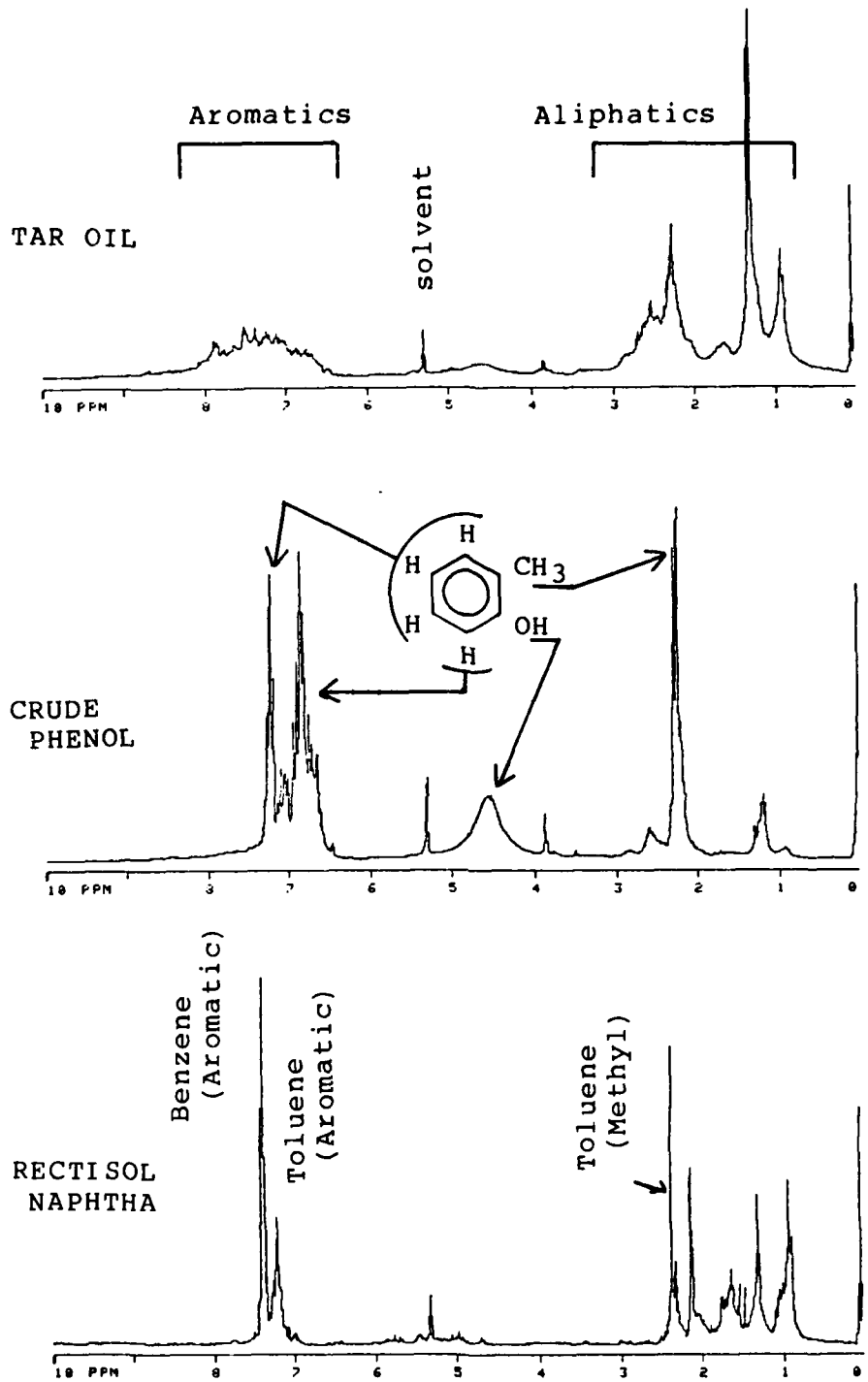


Figure 3. Proton NMR spectra of tar oil, crude phenol, and rectisol naphtha.

TABLE 3

PROTON AND CARBON-13 NMR DATA

Carbon Type	NMR Region ppm	AV Jet A Area %	Tar Oil Area %	Crude Phenol Area %	Rectisol Naphtha Area %
		PROTON NMR			
Aromatic	9.0 - 5.9	4.8	28.3	50.2	38.9
Phenol	4.4 - 3.5	0.4	2.4	16.9	0.4
Acenapthene	3.5 - 3.3	0.1	0.5	2.1	1.9
$-CH_2$-alpha	3.3 - 1.9	6.5	28.4	23.5	22.2
$-CH_2$-beta	1.9 - 1.5	7.8	5.3	1.3	10.5
$-CH_2-$	1.5 - 1.0	43.6	23.4	4.8	13.9
$-CH_3$	1.0 - 0.1	36.8	11.7	1.2	12.2
Total Area %		100.0	100.0	100.0	100.0
$-CH_2-/-CH_3$		1.2	2.0	4.0	1.1
		CARBON-13 NMR			
Aliphatic,C=	240-187	2.5		1.0	2.0
Aromatic,C=O	187-160	2.3		0.1	1.1
Phenolic	160-149	1.0		10.2	0.0
Aromatic,=C=	149-138	2.5		8.3	2.7
Aromatic,=C-	138-95	10.1		65.8	66.7
Methoxyl	95-60	0.1		0.2	1.1
Aliph.,$-CH_2-$	50-36	23.0		1.4	4.3
C	36-27	33.3		2.3	9.7
alpha C	27-17	16.8		5.2	8.0
$-CH_3$	17-0	8.4		5.5	4.4
Total Area %		100.0		100.0	100.0

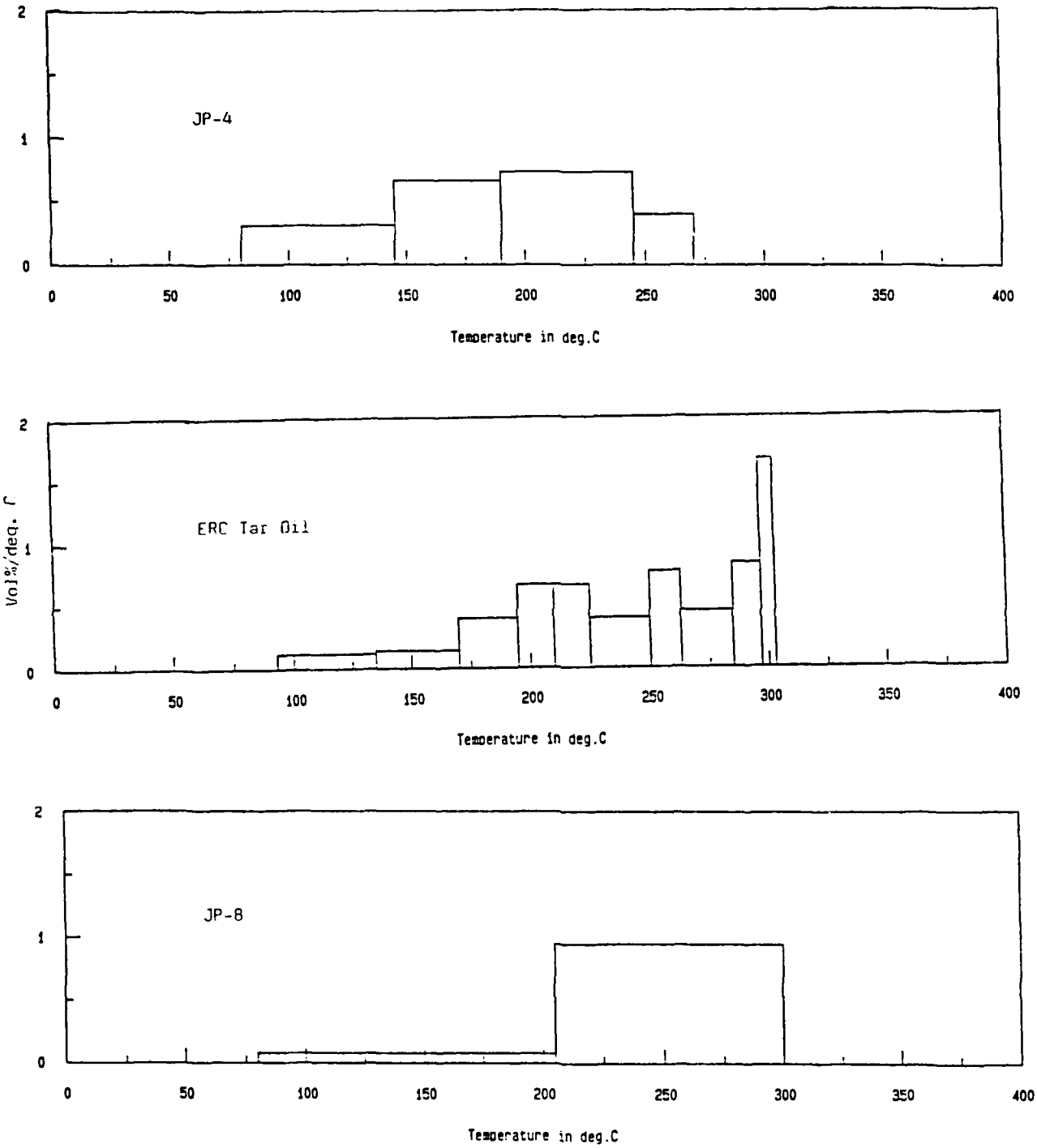


Figure 4. ASTM D86 distillation profiles of specification JP-4, tar oil, and specification JP-8.

EXPERIMENTAL

Various analyses have been performed on the tar oil, crude phenol, and rectisol naphtha streams to provide an overall picture of their physical and chemical properties. The initial samples were obtained from the GPGP. The various analyses performed on one or more of the streams are listed below:

1- Elemental Composition (C,H,N,S)
2- Insolubles, Ash, Water, and Trace Metals Content
3- Sample Volatility
   - D86 Distillation
   - D1160 Distillation
   - GC Simulated Distillation (D2887)
   - True Boiling Point Distillation
4- Component Analyses
   - GC/MS
   - EI,CI
   - GC/FTIR
5- Compound Type Analyses
   - Proton NMR
   - Carbon NMR
   - Short-Column Separation (aliphatics, aromatics, polars)
   - Acid - Base - Neutral Separation

The various analyses provide information necessary to evaluate the various streams even though some of the analyses partially duplicate each other. However, the duplication of data by different analytical techniques provides a higher degree of credibility to the data. The techniques and equipment used as well as experimental limitations will be discussed in this section.

Elemental Composition

The elemental analyzer is a Model 240-XA made by Control Equipment Corporation, of Lowell Massachusetts and can determine the carbon, hydrogen and nitrogen content of volatile and non-volatile liquids and solids. This is a computer controlled instrument equipped with a single automatic sample injector. A Perkin-Elmer Model AD-2Z micro-balance is used for all sample weighing. A sample size of 3 mg was used. The sample was combusted under static conditions in the combustion tube at 950°C. The combustion time could be varied from 60 to 255 seconds to insure the complete oxidation of all organic material. The combustion gases were detected by a series of thermo-conductivity detectors. The instrument was normally calibrated against acetanilide, although other appropriate standards could be used.

Equipment calibrated for the elemental analysis of coal liquids provides high values for carbon and hydrogen when used

with more volatile highly hydrogenated fuels. Therefore, similar known compounds were analyzed before and after volatile fuel samples were analyzed to provide a secondary calibration.

Total sulfur determination was done with a LECO Model 532 sulfur analyzer. The sample (up to 100 mg) was placed in a porous crucible along with iron and tin accelerators and was inductively heated in a stream of oxygen to temperatures reaching 3000°F. The combustion products were continually swept into the titration cell where an iodometric titration of the SO_2 takes place throughout the duration of the burn. The instrument was calibrated against either potassium aluminum sulfate or a standard coal sample of known sulfur content. The method of analysis conforms to ASTM D1551 specifications.

The elemental composition of a sample provides general information about the minimum amount of hydrogen required to upgrade it to a jet fuel, the general structure of the organic substituents, and potential problems due to the presence of heteroatoms.

A minimum amount of hydrogen required to produce a product with a given hydrogen content can be estimated using the elemental data and a general formula which does not include organic gas make.

$$CHNOS + H_2 \longrightarrow CH_n + NH_3 + H_2O + H_2S$$

To improve the estimate, additional knowledge of actual compounds present is required since oxygen could be present in phenolics or in cyclic ethers, the removal of which would consume different amounts of hydrogen. Likewise, different nitrogen- and sulfur-containing compounds would consume more or less hydrogen during their removal. For a tar oil containing 82.62, 8.63, 1.01, 7.27, and 0.47 wt% of C,H,N,O, and S, respectively, about 3100 scf of hydrogen per barrel of feed would be required to process a 95% yield of product containing 13 wt% of hydrogen. About 30% of the hydrogen consumed would be needed to remove the phenolic oxygen. The crude phenol stream which contains 75.57, 7.32, 0.29, 16.78, and 0.04 wt%, respectively, would require a minimum of about 5500 scf of hydrogen gas per barrel of feed to process an 87% yield of product. About 41% of the hydrogen gas consumed would be needed to remove oxygen. The detrimental affect of oxygen on hydrogen consumption and yield is obvious. Removing sulfur also requires hydrogen and reduces the yield of products but to a much lesser extent than oxygen.

Nitrogen content is more detrimental due to its ability to poison catalysts. High nitrogen contents indicate a need to pre-treat the stream to remove the nitrogen compounds or the need to employ special upgrading techniques such as a guard bed of inexpensive catalyst.

The predominance of one or another organic structure is also indicated by the hydrogen and oxygen content of a sample. Alkanes are rich in hydrogen. A ten carbon aliphatic would contain 15.5 wt% hydrogen. As the number of aliphatic carbons increases the hydrogen content approaches 14.3 wt%. A ten carbon naphthene (decalin) contains 13 wt% hydrogen while a ten carbon aromatic (naphthalene) contains only 6.3 wt% hydrogen. Commonly present oxygenated compounds (cresols) contain 7.4 wt% hydrogen and 14.8 wt% oxygen. In general, the likelihood of the presence of aromatics increases rapidly as hydrogen content decreases below 13 wt% while the likelihood of phenolics being present increases rapidly with increasing oxygen content.

D86, D1160, TBP, and Simulated GC Distillation Analysis

The volatility of samples is an important, often used parameter for fuels and is determined by distillation analysis. A number of techniques have been used to determine the volatility of the GPGP byproduct liquid streams. Distillation analyses have also been made in order to provide samples at unique distillation cut points for other analyses to get more detail on the components present.

ASTM D86 and D1160 Analyses

ASTM D86 analyses have been performed on the various streams. This is a simple technique. The analysis is performed at atmospheric pressure and provides about a one plate separation. However, D86 data are widely reported and therefore are the most easily used for interlab comparisons. The data are collected in units of volume percent distilled (vol% over) versus temperature at a certain distillation rate. Weight percent (wt%) data can be estimated using density data, if available. However, errors can occur if densities of different vol% fractions are not measured and are widely different as seen in the example on Table 4.

TABLE 4

CONVERSION OF D86 VOL% DATA TO WT%

Compound	1	2
D86 vol%	50.0	50.0
Density, g/mole	0.8	1.0
Calculated wt%	44.4	55.6

Analysis of collected D86 fractions by gas chromatography indicated that there was a broad overlap of compounds in the various distillation cuts (Figure 5).

As were many techniques, the D86 test was developed for the petroleum industry for use with simple aliphatic and alkylated aromatic compounds. Coal-derived liquids are more diverse since they contain numerous aromatic and phenolic compounds. The presence of water complicates the analysis since many phenolics co-distill (or form azeotropic mixtures) as do some aromatics. This was observed in the initial TBP fraction of the phenol stream.

The initial ASTM D86 distillations of the by-product stream samples (crude phenol, tar oil, and rectisol naphtha) and AV Jet A did not meet specs of the analysis; specifically, achieving a 98.5% recovery. In order to meet specs, the distillation rate was increased and the condenser temperature lowered, which brought the weight loss down below 1.0%. Table 5 shows a comparison between the distillations done at a slow rate to that done at a faster rate. The data shows that the tar oil must be thermally unstable during distillation. As the distillation rate was increased to a point where the weight loss dropped below 1%, the residue increased from less than 10% to greater than 30%, and the final temperature decreased from 303°C to 260°C.

The final temperature of the distillation is determined by the smoke point of the sample or the thermal decomposition point. At this point, smokey vapors are seen in the flask and the vapor temperature begins to fall even when more heat is applied. At the higher pot temperatures associated with the faster heating rate, reactions to form smokey vapors were observed at lower overhead temperatures indicating that the rate of heating influenced the stability of the sample.

As seen, coal liquids can be unstable during distillation. The tar oil stream was found to be particularly unstable resulting in varied amounts of total distillate being recovered. As will be discussed later, the total amount distilled depended mainly on the initial heating rate from 0 to 10 vol% over. Heating rates of over 2°C/min led to low values of distillate.

ASTM D1160 data were obtained for the tar oil stream for comparative purposes. This technique is a vacuum distillation and therefore does not subject the sample to high pot temperatures as do D86 distillations. D86 distillations were appropriate for the naphtha and phenol streams. D1160 was best for the tar oil stream unless one wished to determine the effect of heating rate at atmospheric conditions on distillation.

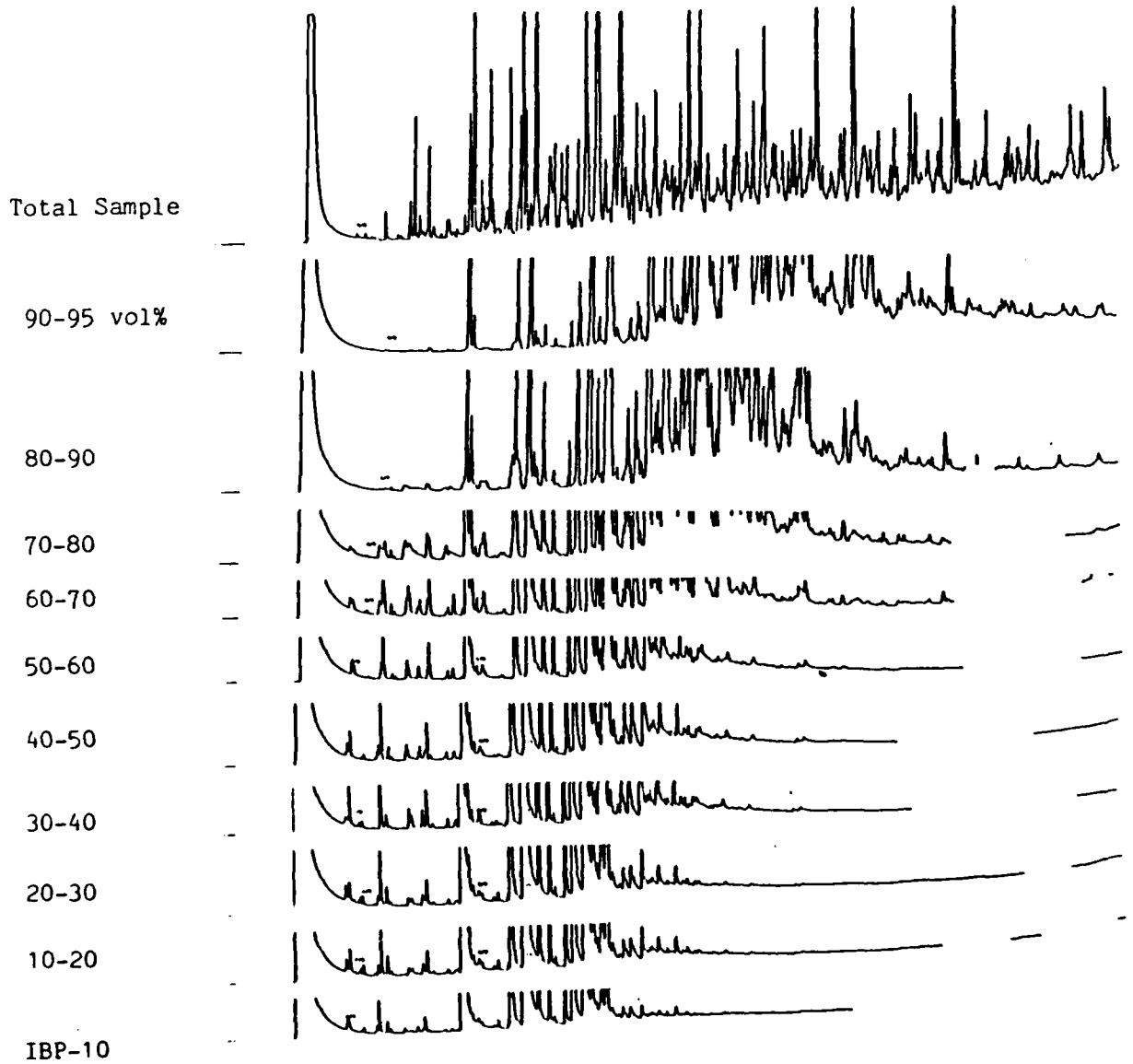


Figure 5. GC analyses of tar oil ASTM D86 distillation fractions.

TABLE 5

EFFECT OF D86 DISTILLATION RATES ON RESIDUE AND LOSS

	Avg. Rate[a]	Condsr. Temp[b]	Min.to IBP[c]	Max. Temp[d]	Resid wt%	Distill wt%	Lost wt%
AV Jet A:							
slow	2.96	55	30	274	2.20	96.21	1.59
fast	3.22	30	16	285	3.31	95.83	0.86
Crude Phenol:							
slow	2.35	55	18	265	5.75	92.45	1.79
fast	3.51	20	9	265	5.45	93.71	0.85
Rectisol Naphtha:							
slow	NA[e]	55	9.5	132	3.53	90.05	6.42
fast	4.67	0	6.6	132	2.80	96.35	0.85
Tar Oil:							
slow	0.99	55	23.5	303	9.66	87.68	2.66
fast	1.89	23	7.8	260	36.93	62.08	0.99

[a]The average rate was in ml/min.
[b]The condenser temperature was in °C.
[c]Minutes to reach the initial boiling point (IBP).
[d]The maximum distillation temperature in °C.
[e]Not available.

GC Simulated Distillation (D2887)

ASTM D2887 distillation analysis uses a gas chromatograph (GC) with a standard column. The GC output is monitored using a thermal conductivity detector (TCD) or a flame ionization detector (FID) which provide data in area percent (area%) for each individual compound. The GC output is fractionated into distillation cut points by comparing it to the output of a series of normal alkanes which have known boiling points. To convert to wt% values, response factors must be used according to equation 1 where Rf is the response factor of compound c.

$$\text{wt\% of a compound} = 100\ (A_c/Rf_c)/\Sigma(A_i/Rf_i)$$

Unfortunately, different compound types and at times different compounds of the same type have very different response factors and all must be known to accurately determine wt% data.

Flame ionization detectors are primarily carbon counters but are most sensitive to CH groups. As seen in Table 6, the range of response factors for alkanes and aromatics which contain no heteroatoms is narrow and area% approximates wt% when assuming an Rf = 1. However, unless response factors are taken into account the concentrations of especially benzene (Rf = 1.12) and toluene (1.07) will be high. For compounds containing heteroatoms response factors as low as 0.54 (diphenolics) and 0.23 (low molecular weight alcohols) are possible. All of the GPGP streams contain numerous compounds that contain heteroatoms. For example, the rectisol naphtha stream contains low boiling oxygenated alkanes such as acetone, the crude phenol stream contains both single and di phenols, and the tar oil stream contains aliphatics, aromatics, and phenolics. To accurately convert GC area% data to wt%, one must identify each GC peak and obtain its response factor, which is time consuming and difficult. An example of the difference of area% and wt% for two types of compounds having response factors of 1.0 (aliphatics and aromatics) and 0.56 (phenol) is shown in Table 7. The amount of phenol present would be 28% low and the amount of aliphatics and aromatics would be 28% high if area% was reported as wt%. Therefore, GC data will be reported in area%.

Other problems exist with simulated GC distillations. Water must be determined separately if an FID is used since it is invisible to the detector. Insolubles, very heavy volatiles, and inorganics will not pass through a GC column and so are not detected. Some compounds, especially diphenolics, are unstable even under GC conditions and may decompose or polymerize and not be detected.

TABLE 6

RESPONSE FACTORS OF VARIOUS HYDROCARBONS

Compound	Response Factor
Aliphatics[a]	0.96 to 1.05
2,3,5-Trimethylhexane	0.96
Heptane	1.00
Isopentane	1.05
Aromatics[a]	0.97 to 1.12
1,2,4-Trimethylbenzene	0.97
para-Xylene	1.00
Toluene	1.07
Benzene	1.12
Oxygenated Aliphatics[a]	0.01 to 0.85
Formic acid	0.01
Methyl alcohol	0.23
Ethyl alcohol	0.46
Acetone (ketone)	0.49
n-Proponal	0.60
Octyl alcohol	0.85
Oxygenated Aromatics[b]	
Phenol	0.56
p-Cresol	0.69
Catechol	0.54
Nitrogenated Aromatics	
Aniline[a]	0.75
Pyridine[b]	0.72
Quinoline[b]	0.76

a) W.A. Dietz, J. of G.C., Feb, 1967, p68.
b) S. Hawthorne and D. Miller, UNDEMRC, private communication.

TABLE 7

CONVERSION OF GC AREA% DATA TO WT%

Compound	1	2
GC area%	50.0	50.0
Response Factor	1.0	0.56
Calculated wt%	35.9	64.1

True Boiling Point (TBP) Distillation

True Boiling Point (TBP) distillations provide a more accurate picture of the separability of a complex mixture by distillation. This technique can be complimented by collecting fractions at selected temperatures and analyzing the individual fractions using gas chromatography. Comparison of the data for each fraction enables the determination of compound purity in each fraction. The crude phenol stream was subjected to TBP distribution analysis. The following describes the calibration of the equipment used to perform the distillation.

The fractional distillation apparatus used to do the TBP distillation had a fractionating column with 12.5 theoretical plates. The column consisted of a 10-inch by 1 1/8-inch OD column packed with 1/4-inch stainless steel springs followed by three 12-inch sections of bubble cap columns. Each bubble cap column section contained 2 inches of stainless steel spring packing at the top and three bubble caps at 2-inch intervals. The receiver was 100 ml in volume and graduated in 1 ml divisions. It had a stopcock drain for collection of individual fractions.

The determination of the number of theoretical plates produced by this column was accomplished by distilling a solution of 50 mole % cyclohexane in toluene and determining the composition of the distillate and boiler contents by gas chromatography. The number of theoretical plates for the column was calculated using Equation 2.

$$(Y1/Y2) = (X1/X2)A^{n+1} \qquad [2$$

where (Y1/Y2) is the mole% ratio of compounds in the distillate. Y1 represents the mole% cyclohexane (lower boiling component) and Y2 the mole% toluene. Likewise, (X1/X2) is the mole% ratio of components in the boiler. X1 represents the mole% cyclohexane and

X2 the mole% toluene. The value n is the number of theoretical plates and A is the partition coefficient. The partition coefficient (A) can be estimated from the boiling points of the two components using Equation 3.

$$\log(A) = 8.9(T2-T1)/(T2+T1) \qquad [3$$

where T2 is the boiling point of component 2 in ^{O}K and T1 the boiling point of component 1 in ^{O}K. Cyclohexane has a boiling point of 80.7^{O}C (353.8^{O}K) and toluene has a boiling point of 110.6^{O}C (383.7^{O}K). A partition coefficient of 2.3 was estimated from Equation 3.

The cyclohexane/toluene solution was distilled at a rate in which the distillate refluxed in the fractionating column for approximately 90 minutes before coming over into the receiver. The first 15% of the distillate was discarded and the next 10% was collected for analysis. As soon as these distillate fractions were collected, the distillation was stopped and the contents of the boiler was immediately sampled. GC analysis of the boiler contents gave a toluene concentration of 74.56 % and cyclohexane was taken by difference as 25.44 %. The distillate analysis showed 0.0043 % toluene (99.9957 % cyclohexane by difference). These results yield a theoretical plate count of 12.5 from Equation 2.

When distilling the crude phenol stream, it was necessary to wrap the fractionating column with heat tape in order to maintain the temperature in the column and to keep the distillation going. In order to insure that the heat applied to the column had a minimum effect, if any, on the number of theoretical plates generated, it was kept low enough so that the distillation rate would stay around 1 ml per minute.

Component Analysis (GC/MS)

Gas chromatography separation with a flame ionization detector (GC/FID), and gas chromatography separation followed by mass spectrometry analysis (GC/MS) can provide detailed information about individual compounds present in complex mixtures. The total tar oil, crude phenol, and rectisol naphtha streams as well as sample fractions obtained from distillations or other separations have been analyzed for component identification. A Hewlett-Packard Model 5985B GC/MS equipped with dual electron impact/chemical ionization sources (EI/CI) was used to obtain the mass spectra used for identification of components in the various samples. Gas chromatographic separations were performed on a Hewlett-Packard Model 5890 (FID) or a Model 5985 GC/MS equipped with a 60 m x 0.25 mm i.d. DB-5 fused silica capillary column (J&W Scientific, Folsom, Calif.).

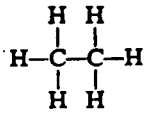
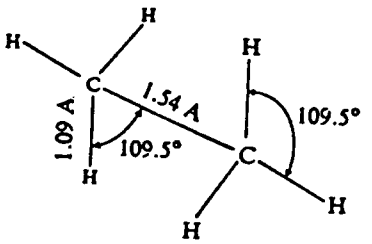
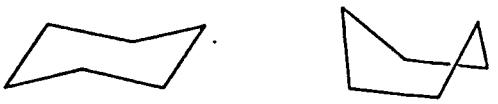
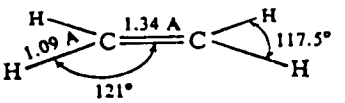
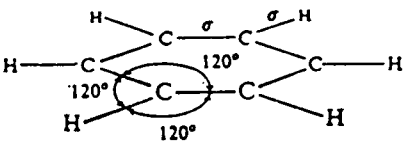
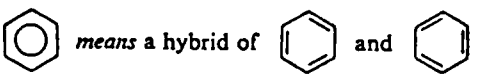
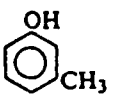
Tar oil and crude phenol samples were diluted with methylene chloride and the diluted samples were injected at 60°C followed by temperature programming to 320°C at 6°C/min. The more volatile rectisol naphtha was injected neat. GC/FID output is in area% of the total area detected versus retention time. Water, most common inorganics and other non-volatile components, as well as organic compounds in concentrations lower than the set FID threshold limit are not counted in the total area percent. Accurate concentrations can be determined using internal standards. For coal derived liquids, care must be taken when using response factors due to the complexity of the mixtures.

Numerous compounds have been identified using MS spectra of individual GC peaks and by their retention indices. Table 8 details some general carbon bonding information as well as names and structures of organic compounds. Compounds like benzene and toluene (methylbenzene) are readily identified by their unique characteristic mass spectra. However, xylenes (dimethylbenzenes) have three possible structures or isomers: ortho-xylene (1,2-dimethylbenzene), meta-xylene (1,3-dimethylbenzene), and para-xylene (1,4-dimethylbenzene). The xylenes can be generically termed C2-benzenes and have elemental formulas of C_8H_{10}. Therefore, they produce identical mass spectra, but do vary somewhat in retention indices. The meta- and para-isomers have a retention index of 869 and can not be distinguished while ortho-xylene has a retention index of 890. A compound of the same molecular weight and also a C2-benzene (ethylbenzene) can similarly be distinguished as different since it has a retention index of 860.

Retention index (Ri) values relate retention times to a standard scale and are used in identifications since they are more independent of GC operating conditions such as gas flow rate and column temperature. The standard scale is based on the retention times of a series of normal alkanes. The normal alkanes are arbitrarily assigned retention indices by multiplying their carbon number by 100; so C9 and C10 have retention indices of 900 and 1000, respectively. Therefore, if an unknown compound has a retention time that falls halfway between the retention times of C9 and C10, the retention index of the compound would have a value of 950. Figure 6 depicts the relationship of retention index values to temperature. Unfortunately, the relationship is not linear since the boiling points of n-alkanes are not linear with the number of carbon atoms in the alkane. However, plots similar to those obtained from D86 distillation data can be obtained from GC component data. Figure 7 depicts the D86 data for the phenol stream and GC component data. The GC data is the cumulative area% of compounds plotted against their boiling point. Adding a correction for water would improve the correlation.

TABLE 8

MAJOR TYPES OF ORGANIC COMPOUNDS

Type	Example	Symbol
ALKANES	Ethane C_2H_6 or CH_3CH_3	 
Cycloalkanes	Cyclohexane C_6H_{14}	 Chair conformation Boat conformation *An energy maximum*
Olefins	Ethylene C_2H_4 or $CH_2{=}CH_12$	
AROMATICS	Benzene C_6H_6	  *means* a hybrid of and
Phenolics	Phenol C_6H_5OH	
Cresols	m-Cresol $C_6H_4OHCH_3$	
HETEROCYCLICS	Furan	
	Pyridine	
	Thiophene	

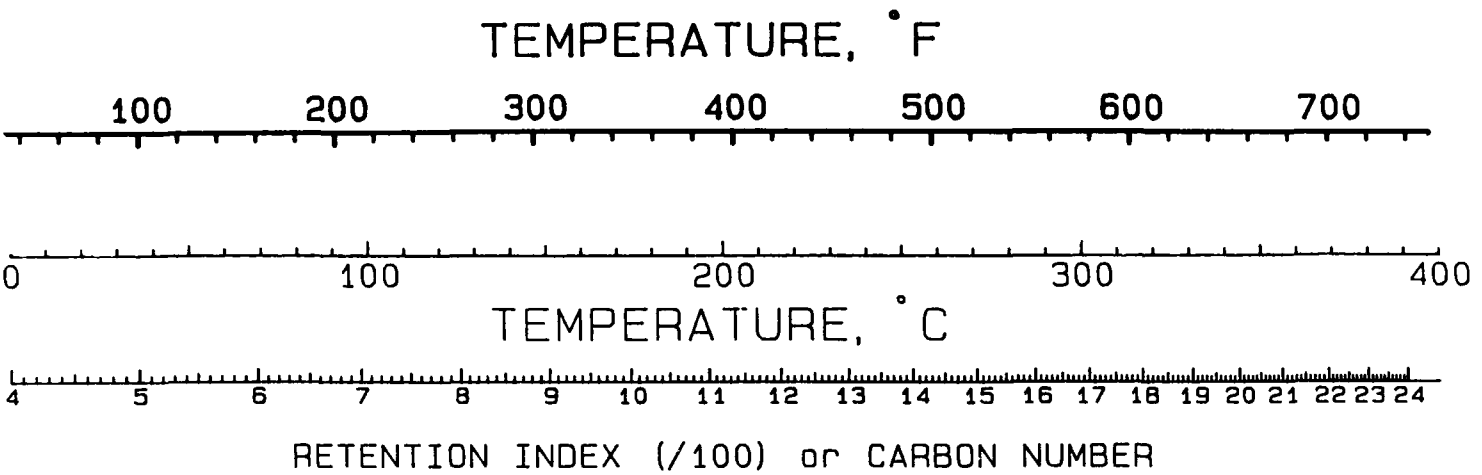


Figure 6. Relationship between retention index / 100 (carbon number) and temperature, compound boiling points (^{o}C and ^{o}F).

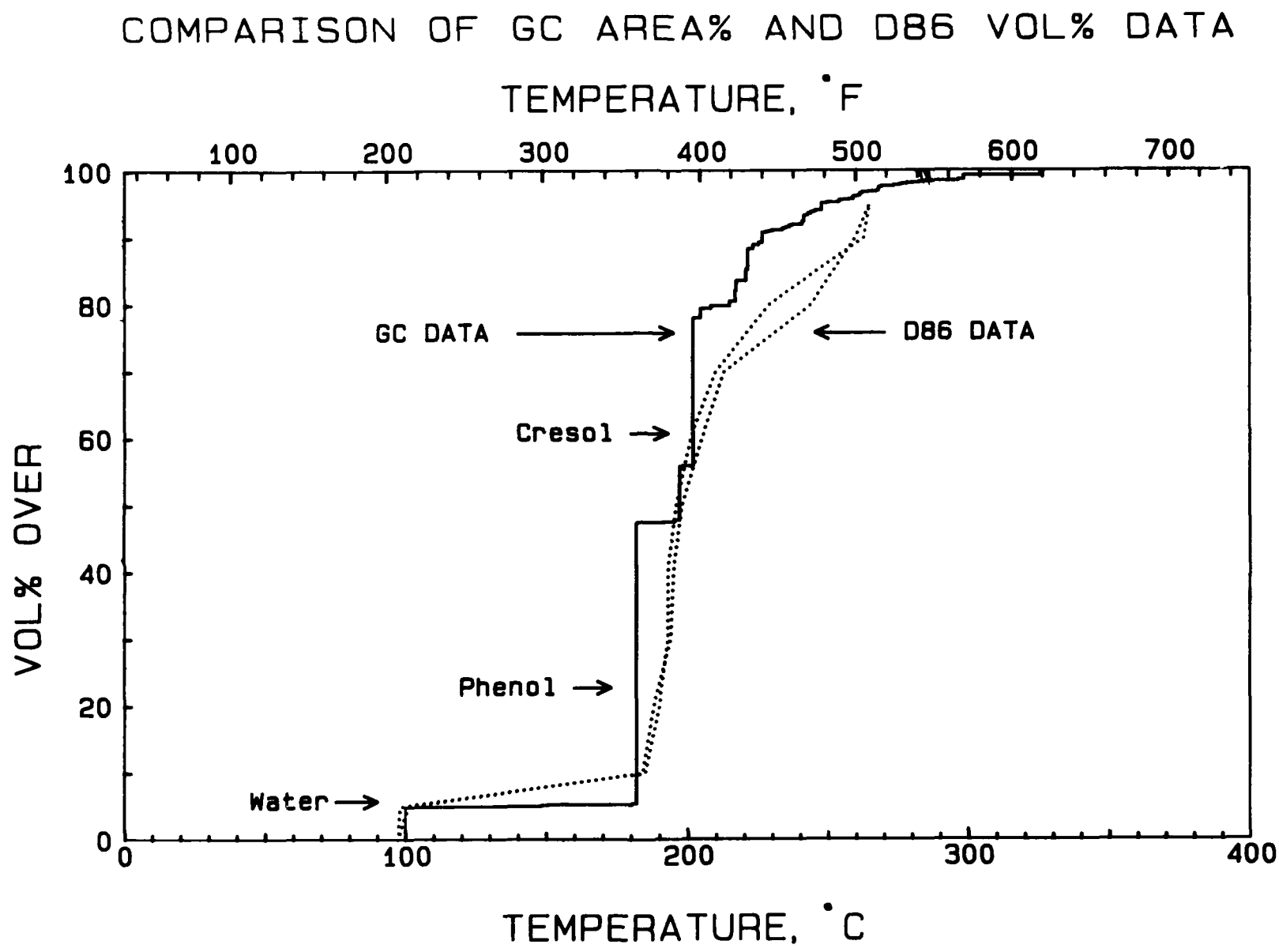


Figure 7. Cumulative GC area% profile and D86 profile for the crude phenol stream.

NMR Analysis

Proton and C-13 data provide information about the hydrogen atoms surrounding carbon and the carbon structure itself. A proton NMR spectrum is a plot of the frequencies at which hydrogen atoms absorb magnetic energy and resonate versus intensity. The resonance frequency can be reported in ppm units from an internal standard, tetramethylsilane (TMS) at zero ppm. The frequency at which a particular hydrogen is observed depends on its position in an organic compound. Table 9 indicates where protons of selected carbon compounds would be observed in a spectrum. NMR spectra of pure compounds can be used to obtain absolute structural information. In complex mixtures, compound type information is obtained. The intensity or area% of a peak is proportional to the number of protons present in the peak relative to the total number of protons observed by the NMR spectrophotometer. Easily exchanged protons such as in the tar acid phenolic groups result in broad peaks or are not observed. The proton NMR spectra were obtained using a Varian XL200 NMR spectrometer at 200 MHz. The pulse width was set for a 90^{o} flip angle. A 3 second acquisition time and a 5 second recycle delay time were used. Spectral width was 2600 Hz and 100 pulses were accumulated for each spectrum. The samples were prepared in deuterated methylene chloride which contained 0.25% TMS. All chemical shift data are presented from TMS at 0 ppm. The residual peak for non-deuterated methylene chloride solvent is observed at about 5.3 ppm.

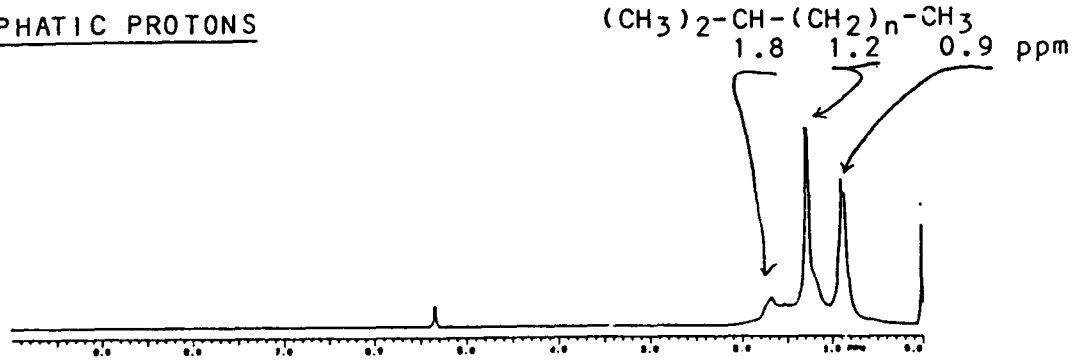
The Varian XL200 NMR is a high field multinuclear instrument. The 47K Gauss magnet has a wide bore and a super-conducting solenoid which operates at liquid helium temperatures. The proton/F-19, 5 mm probe observes protons at 200 MHz and the 10 mm broad band probe can observe C-13 at 50 MHz and a variety of other nuclei at their respective frequencies. Cross polarization/magic angle spinning solid state C-13 NMR utilizes a Doty Scientific solids probe which spins the sample in a sapphire rotor at 3.5 to 4 KHz. A high power decoupler amplifier is used for proton decoupling of the carbon spectra in the solid state. The solids probe is broad band tunable with different wands available to observe nuclei other than carbon. The data system is an Advance System update by Varian. It has a Host System Motorola CPU with 32 bit registers and arithmetic operations/16-bit data transfer, 16K byte ROM, 128K byte dual-ported RAM, VERSA bus system interconnect with IO interface and an Acquisition System CPU with the same capacity plus interface to the pulse sequence controller. Any pulse sequence may be used. All spectra are stored on 5.25-inch floppy disks.

For complex mixtures containing many different compounds, proton NMR spectra of the mixture provide semi-quantitative data of functionalities present. However, in less complicated mixtures, one can often determine semi-quantitatively

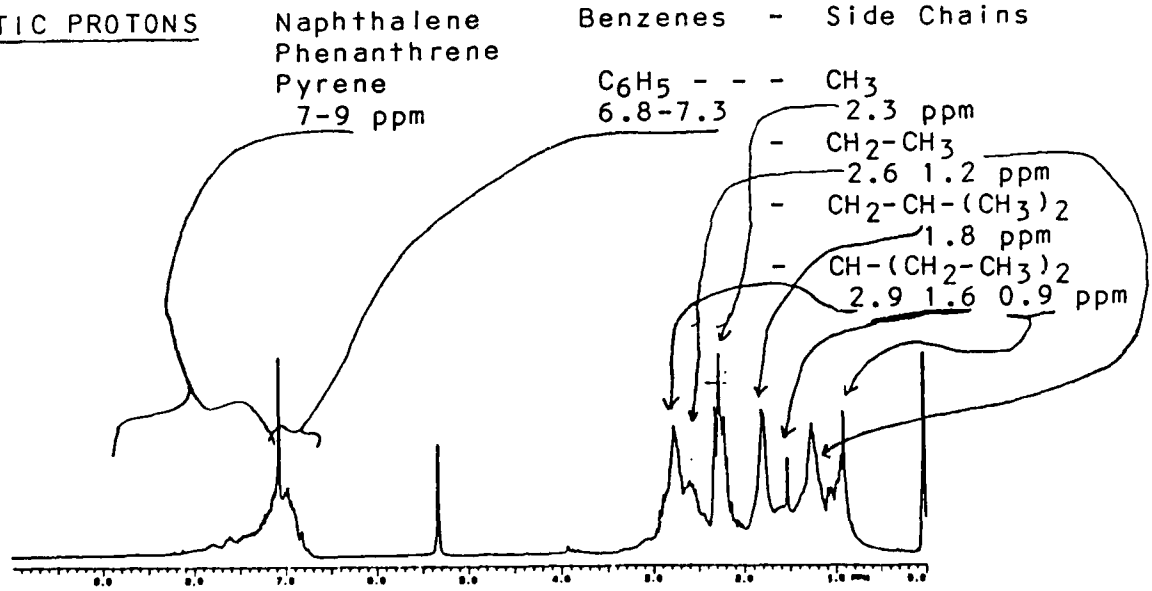
TABLE 9

PROTON NMR ABSORPTION REGIONS

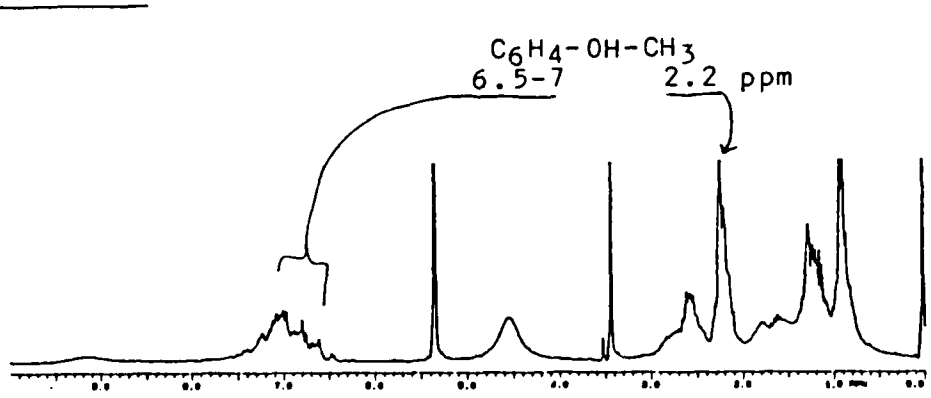
ALIPHATIC PROTONS



AROMATIC PROTONS



POLAR PROTONS



concentrations of individual compounds. Unique protons in phenol, the cresols, and methoxy-compounds exist which can be readily observed in unique positions in proton NMR spectra as seen in Table 10. Phenol has only one hydroxyl and five aromatic protons which resonate in unique regions. Cresols also have a hydroxyl proton but only four aromatic protons and three protons on a carbon atom alpha to the aromatic ring (alpha methyl group). The hydroxyl and aromatic protons of the cresols resonate in similar regions as do the ones in phenol but the methyl protons resonate in a unique region. Protons in the methyl group of a methoxyl functionality also resonate in a unique region. The presence of peaks in specific NMR regions and the absence of peaks in other NMR regions can be used to estimate the purity of a sample and in simple mixtures, semi-quantitative concentration data can be calculated for each component using the peak area percent values.

The proton NMR spectra of the total crude phenol stream is presented in Figure 8 for the as received wet sample (Figure 8a) and for the same sample after drying (Figure 8b). The sample was dried by dessicating it with type 4A molecular sieves which absorb water. The drying is necessary since the hydroxyl proton can hydrogen bond with water and exchange with water protons causing the hydroxyl proton peak between 4.4 to 5.5 ppm to be very broad and to overlap with the methylene chloride solvent peak which lies between 5.2-5.9 ppm. The NMR data for the total sample and the wet and dry samples for the 9 fractions are presented in Tables 11 and 12 for comparison. The NMR regions for and descriptions of the various protons are:

Aromatic protons (9.0-7.0 ppm),

Phenolic aromatic protons (7.0-5.9 ppm) are attached to aromatic carbons adjacent to the oxygen-bound carbon of a phenol,

Phenolic OH protons (4.4-5.2 ppm) are attached to the oxygen in a phenolic compound (the peak shape and position are greatly influenced by water),

Methoxyl protons (4.4-3.5 ppm) are the protons in the methyl group,

Acenaphthene protons (3.5-3.3 ppm) are attached to the bridge carbon atom in acenaphthene-like compounds,

Alpha to Aromatic protons (3.3-1.9 ppm) or alpha-methyl protons are attached to a carbon adjacent to an aromatic ring,

Beta to Aromatic protons (1.9-1.5 ppm) are attached to a carbon once removed from an aromatic ring,

Methylene protons (1.5-1.0 ppm) are atached to carbon atoms in alkanes or in long alkyl side chains, and

TABLE 10

PROTON NMR RESONANCES OF PURE PHENOLIC COMPOUNDS

	B.P.	Chemical Shift[a]			Proton Area%			
		OH	CH_3	OCH_3	Arom	OH	CH_3	OCH_3
Phenol	182	4.82	--	--	83.3	16.7	--	--
o-Cresol	191	4.79	2.25	--	50.0	12.5	37.5	--
m-Cresol	202.8	5.17	2.29	--	50.0	12.5	37.5	--
p-Cresol	201.9	4.77	2.27	--	50.0	12.5	37.5	--
2,3-Dimethyl phenol	218	4.62	2.27 2.16	--	30.0	10.0	60.0	--
2,4-Dimethyl phenol	212	4.58	2.24 2.21	--	30.0	10.0	60.0	--
2,5-Dimethyl phenol	242	4.53	2.27 2.21	--	30.0	10.0	60.0	--
Guaiacol (2-Methoxy phenol)	205	5.66	--	3.87	50.0	12.5	--	37.5
Anisole (Methoxybenzene)	153.8	--	--	3.80	62.5	--	--	37.5
o-Methyl anisole	171.3	--	2.22	3.82	40.0	--	30.0	30.0
p-Methyl anisole	177.2	--	2.29	3.78	40.0	--	30.0	30.0
Resorcinol (1,3-Dihydroxybenzene)	244.3	4.76	--	--	66.7	33.3	--	--
Catechol (1,2-Dihydroxybenzene)	240	5.15	--	--	66.7	33.3	--	--
Hydroquinone (1,4-Dihydroxybenzene)	285	4.42	--	--	66.7	33.3	--	--

[a] The chemical shift was measured in ppm from tetramethylsilane.

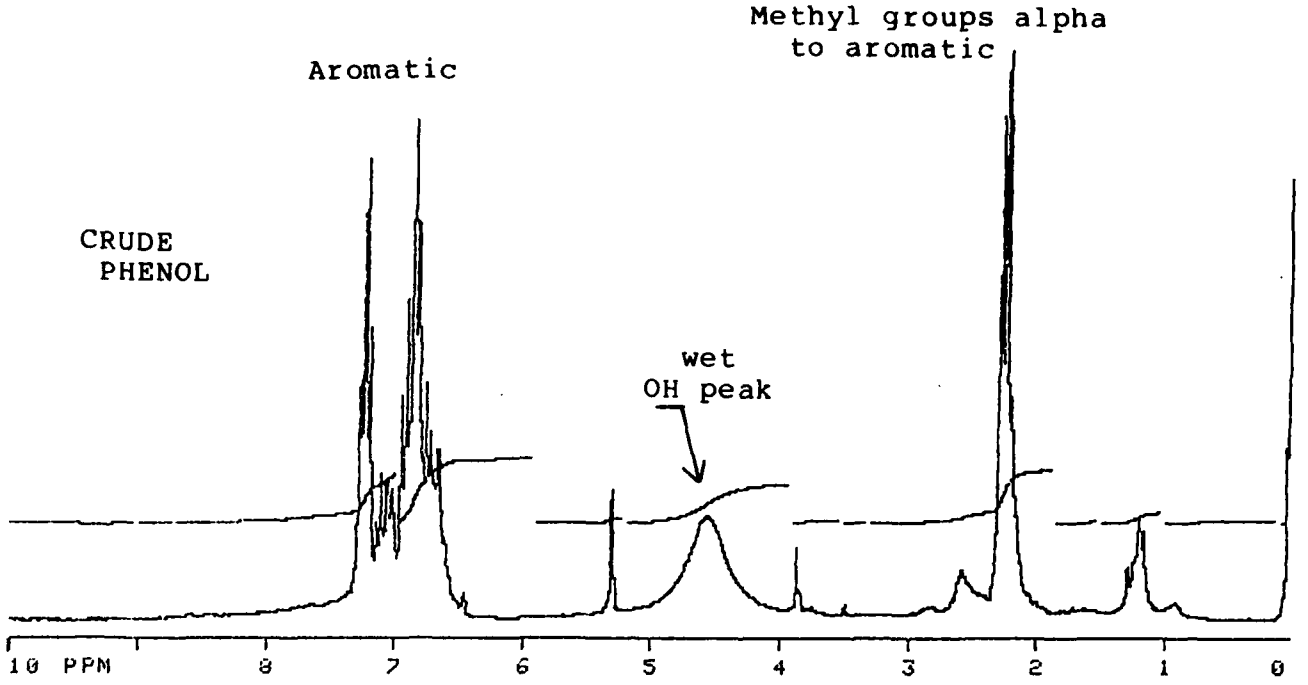


Figure 8a. Proton NMR spectrum of the crude phenol stream.

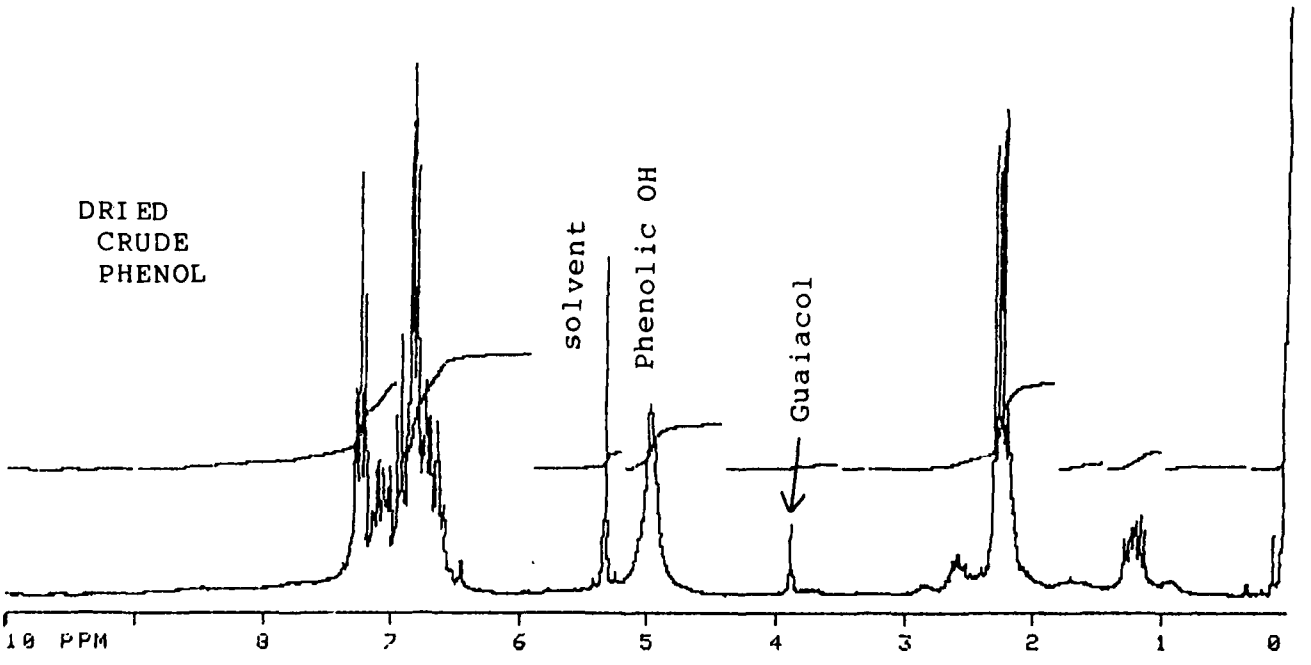


Figure 8b. Proton NMR spectrum of the crude phenol stream after drying with Type 4A molecular sieves.

TABLE 11

PROTON NMR DATA AND FUNCTIONAL GROUP ANALYSES FOR THE DRIED GPGP PHENOL STREAM

Functional Group	NMR Region ppm	Total Proton Area%	Sum of Proton Area%
Aromatic	9.0-5.9	54.8	50.1
Phenolic	5.2-4.4	12.2	12.0
Methoxyl	4.4-3.5	1.3	2.0
Alpha-Methyl	3.3-1.9	23.6	24.2
Other	-	8.0	10.3
Total	-	99.9	98.6

TABLE 12

PROTON NMR OF CRUDE PHENOL FRACTIONS[a]

		Fraction 1 IBP-178°C, 7.14 wt%		Fraction 2 178-179°C, 10.96 wt%		Fraction 3 179-180°C, 9.75 wt%		Fraction 4 180-181°C, 9.26 wt%		Fraction 5 181-190°C, 6.5 wt%	
	ppm	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
Aromatic	9.0-7.0	16.0	16.4	34.2	35.5	32.0	37.7	33.8	33.5	31.8	29.1
Phenolic Arom.	7.0-5.9	14.2	13.7	41.7	41.8	39.9	37.4	38.9	39.2	32.5	33.7
Phenolic OH	5.2-4.4	1.3	4.0	14.9	15.4	15.8	15.2	14.8	15.3	12.4	13.5
Methoxy	4.4-3.5	9.9	5.8	1.2	0.9	1.3	0.6	0.9	1.0	1.3	1.5
Acenaph.	3.5-3.3	2.5	0.8	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.2
Alpha to Arom.	3.3-1.9	21.6	21.7	4.7	3.9	6.7	6.4	8.2	8.2	18.5	19.0
Beta to Arom.	1.9-1.5	3.7	4.0	1.0	0.7	2.3	0.9	1.4	0.9	1.0	0.9
Methylene	1.5-1.0	24.6	27.2	1.2	1.0	0.9	0.9	0.9	0.8	1.1	1.0
Methyl	1.0-0.2	6.3	6.4	1.1	0.7	0.8	0.7	0.9	0.8	1.1	1.0
		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[a] Dried samples were desiccated with type 4A molecular sieves.

TABLE 12 (cont.)

		Fraction 6 190-193°C, 3.65 wt%		Fraction 7 193-198°C, 13.08 wt%		Fraction 8 198-202°C, 5.16 wt.%		Fraction 9 Pot residue	
	ppm	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
Aromatic	9.0-7.0	25.3	24.7	20.2	21.1	18.3	17.6	9.2	10.8
Phenolic Arom.	7.0-5.9	28.3	27.9	27.0	26.0	25.7	26.4	23.4	22.4
Phenolic OH	5.2-4.4	9.4	11.0	9.8	10.9	7.6	10.5	10.3	11.8
Methoxy	4.4-3.5	2.1	2.0	3.7	3.1	4.4	3.7	2.6	1.6
Acenaph.	3.5-3.3	0.3	0.4	0.4	0.3	0.4	0.2	0.3	0.0
Alpha to Arom.	3.3-1.9	31.7	31.0	34.8	35.1	38.6	37.1	37.1	36.2
Beta to Arom.	1.9-1.5	0.6	0.6	0.6	0.4	0.6	0.3	3.5	3.4
Methylene	1.5-1.0	1.3	1.5	1.9	1.9	3.3	3.0	10.8	11.2
Methyl	1.0-0.2	0.9	1.0	1.7	1.3	1.0	1.1	2.8	2.7
		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Methyl protons (1.0-0.2 ppm) are attached to carbon atoms in the terminal positions of alkanes or alkyl side chains over 2 carbon atoms long.

In comparing the data for wet and dry samples it can be seen that drying had little influence on the area percents observed for the proton types in the various fractions. The proton area% data for the total sample could not have been obtained without drying due to the overlap of the phenolic OH peak with the methylene chloride solvent peak.

Short Column Separations (aliphatic, aromatic, and polars)

Crude phenols, tar oil, and AV Jet A samples have been separated into aliphatics, aromatics, and polars by solvent elution from a silica gel column. The separation of complex mixtures into compound-type fractions which can be weighed followed by analysis of the fractions enables better comparisons of different mixtures. A short column separation technique was used to obtain fractions of compound types. Aldrich grade 12, 28-200 mesh silica gel was activated by heating at 250°C for 15 hours. After cooling, the gel was loosely packed into a 1.5 cm i.d. glass chromatography column to a bed height of about 47.0 cm. At the bottom of the column was a fritted glass filter directly above a narrow bore opening which reduced the flow through the column. After weighing out an approximately 1.0 g sample, the column was flushed with pentane. When pentane began to flow out the bottom of the column, the sample was placed on the silica gel at the top of the column. The sample was then eluted with 1) 150 ml of pentane (simple aliphatics fraction), 2) 50 ml of iso-octane and then 50 ml of pentane (cyclic aliphatic fraction), 3) 250 ml of methylene chloride (aromatic fraction), and 4) 100 ml of methanol (polar fraction). The four fractions were collected in separate, preweighed flasks. In order to determine quantitative yields, the solvents were evaporated using a Roto-vap vacuum evaporation system and weighed. This enables the determination of any loss of light or adsorbed materials. The aliphatic fractions (1 and 2) were usually combined to give just one aliphatic fraction. If the recovery showed a high loss, the light ends (IBP to 140°C) were stripped off prior to the short-column separation and analyzed separately.

Acid - Base - Neutral Separations

The tar oil and crude phenol streams were separated into acid, base, and neutral fractions which were subsequently analyzed by GC/MS in order to obtain additional information about the compounds present. The base fraction is most interesting since it concentrates the nitrogen base compounds.

In this separation technique 15 g of sample were initially

extracted with 200 ml of n-pentane. For the tar oil sample some insolubles were present and therefore removed. The initial pentane layer was then extracted with three 50 ml portions of 2M NaOH to extract the acids (mainly phenolics) into the sodium hydroxide solution. The aqueous solution was neutralized and the acids were removed by extraction with pentane. The pentane was removed by evaporation to give a weighable acid fraction.

The initial pentane layer was then extracted with 2M HCl to extract bases (mainly nitrogen containing compounds) following the same procedure as was used with the NaOH extraction. The aqueous layer was neutralized to pH 12 with 20% NaOH and extracted with three 75 ml portions of methylene chloride to obtain the base fraction. The methylene chloride was then removed by evaporation. From the tar oil stream 0.4 g of bases (2.6 wt%) were recovered for further analysis.

The neutral fraction was recovered by evaporation of the pentane extraction solvent. Mass recoveries for this technique have been lower due to losses in discarded aqueous layers, any losses of pentane insolubles (the initial tar oil contained 2-4 wt% water) in the initial pentane extraction, and any volatile matter removed during evaporation of extracting solvents. However, the material extracted was present in the original sample as were the compounds identified during subsequent GC/MS analysis.

TAR OIL STREAM

The tar oil stream has the greatest potential to be used as a feedstock to produce jet fuel. However, it is a thermally unstable material containing myriads of compounds. Numerous elemental and distillation analyses have been performed. The tar oil stream has been separated into four compound types to provide more information: aliphatics, aromatics or neutrals, polars or acids, and bases. The wt% of each compound type or fraction in the total tar oil has been determined. Nuclear magnetic resonance (NMR), and gas chromatography-mass spectrometry (GC/MS) techniques have been used to provide detail as to what compounds and at what concentration they are present in the fractions. Elemental analysis on the total sample and each fraction enable, mass balancing.

Tar Oil Elemental and Composition Data

The tar oil stream has been analyzed by a number of laboratories and comparative data are presented in Table 13. The metals and ash contents of the tar oil are presented on Table 14.

TABLE 13

TAR OIL ELEMENTAL ANALYSIS[a,b]

NO. SAMPLE	1 ERC1		2 ERC2		3 ERC3		4 ANG1		5 ANG2		6 WRI1		7 WRI2	
	AR	mf	AR[e]	mf	AR	mf[e]	AR	mf[e]	AR[e]	mf[e]	AR	mf	AR	mf
wt% C	NA	82.60	83.76	84.78	80.48	83.70	86.00	87.75	85.98	87.70	82.25	83.50	83.15	84.33
H		8.63	8.83	8.80	8.89	8.80	8.50	8.45	8.65	8.60	8.60	8.56	8.70	8.66
N		1.01	0.52	0.53	0.67	0.70	0.50	0.51	0.59	0.60	0.82	0.83	0.82	0.83
S		0.47	0.39	0.39	0.29	0.30	0.40	0.41	0.39	0.40	0.51	0.52	0.54	0.55
O[d]		7.29	6.50	5.12	9.41	6.50	4.60	2.48	4.01	2.70	7.82	6.59	6.79	5.63
total		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
water			1.20		4.00		2.00		2.00					

[a]Data obtained from various references as listed below.
[b]AR is as received and mf is moisture free, NA means not analyzed or not available.
[e]Calculated data
[d]Includes any ash

No. 1-3: EMRC 2nd qtrly Table 2.2, and 2nd qtrly Table 2.1, 1st qtrly Table 1, respectively.
No. 4-5: ANG memorandums dated 9/16/86 and 1/26/87 respectively.
No. 6-7: WRI qtrly, 3/11/87, Table 1, samples 86-72A and 86-72B, respectively.

TABLE 14

METALS AND ASH CONTENTS OF TAR OIL STREAM

Ash	Ø.2 wt%
Water	4.4
Vanadium	not detected
Nickel	5 ppm
Iron	14Ø
Density	1.Ø25 g/ml

Tar Oil Distillation Data

ASTM D86 Distillation Data

Evaluation of simple ASTM D86 distillation data demonstrates the thermal instability of the tar oils. As depicted in Figure 9, the distillation curves and corresponding final boiling point can vary dramatically. The primary factor affecting this variability is the rate of heating of the sample. Figure 1Ø depicts data from different laboratories (average data from ANG Coal Gasification Company, Western Research Institute, and the UND Energy and Mineral Research Center) for D86 data for the same original sample. Table 15 presents the tabulated D86 distillation data. As will be discussed, end point differences are probably due to differences in the heating rate.

Although rapid distillations led to low distillate yields, it was possible to obtain a high yield with distillations where the heating rate was about 2.5°C/min. This enabled the collection of individual distillate cuts which could be analyzed to obtain more information about the tar oil stream. The data for the various distillate fractions are presented in Table 16. It can be seen that in the tar oil stream the oxygen content is highest in the 207°C cut where phenolics distill and is lowest in the residue. The hydrogen content decreases to a minimum in the residue which contains only 4.9 wt%. Nitrogen content is also highest in the residue and any coal fines (THF insolubles) would concentrate in the residue.

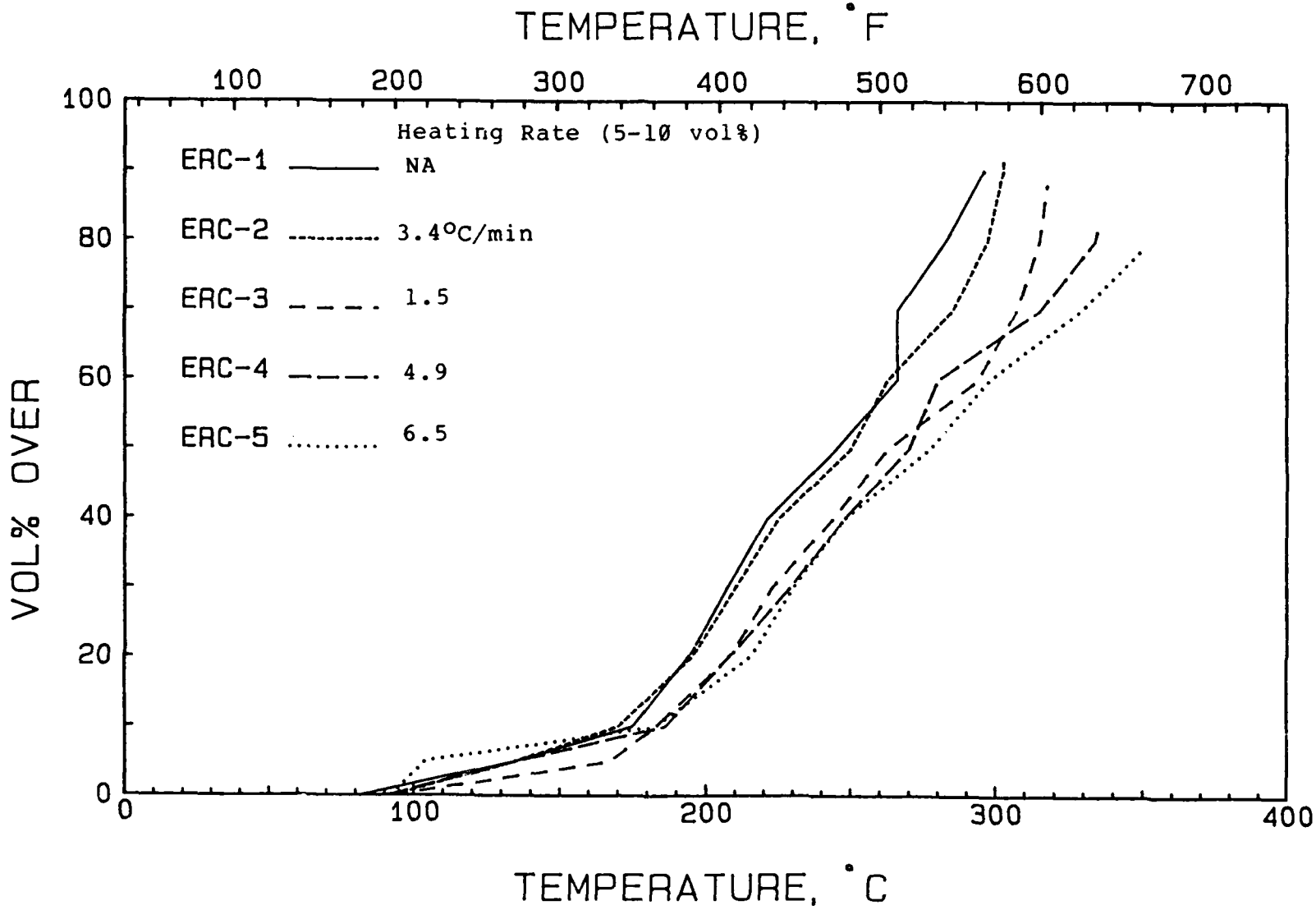


Figure 9. Cumulative volume % versus temperature in °C(°F) for ERC tar oil D-86 distillation data.

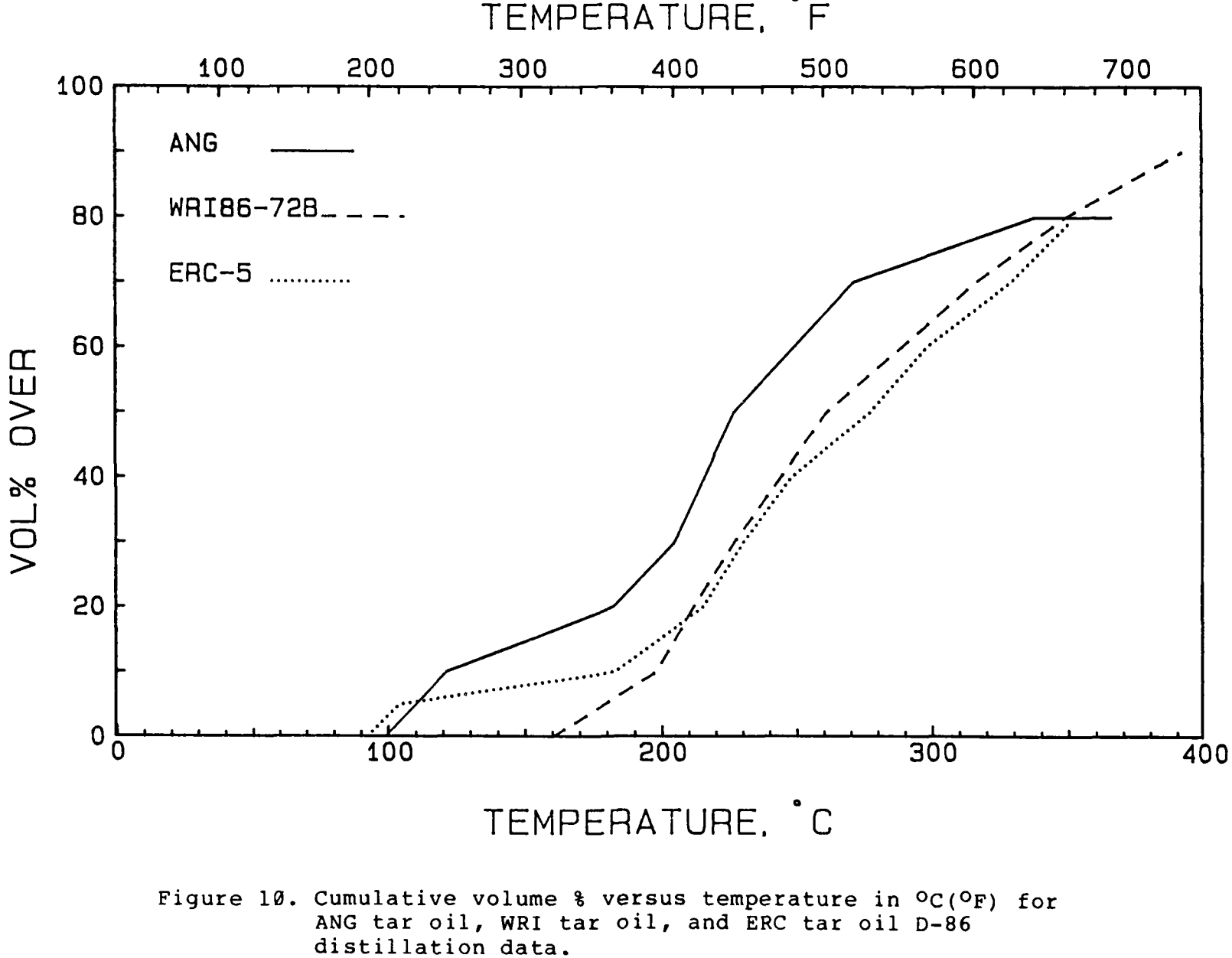


Figure 10. Cumulative volume % versus temperature in °C(°F) for ANG tar oil, WRI tar oil, and ERC tar oil D-86 distillation data.

TABLE 15

TAR OIL D86 DISTILLATION DATA[a]

NO. SAMPLE	1 ERC1		2 ERC2		3 ERC3		4 ERC4		5 ERC5		6 ANG2		7 WRI1		8 WRI2	
Sp Gr	1.025		1.015		NA		1.010		1.010		1.014		1.018		1.018	
ASTM D86	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F
IBP	82	180	93	199	93	199	91	196	92	198	99	210	135	275	160	320
5	135	275	135	275	167	333	135	275	104	219	121	250				
10	175	347	170	338	183	361	186	367	183	361	182	360	193	379	198	388
20	194	381	195	383	208	406	208	406	215	419	204	400	209	409	212	413
30	207	405	210	410	223	433	229	444	230	446	227	440	228	443	227	440
40	221	430	225	437	244	471	248	478	248	478						
50	245	473	250	482	263	505	270	518	277	531	271	520	284	544	261	502
60	266	511	263	505	294	561	280	536	298	568						
70	266	511	285	545	307	585	315	599	329	624	338	640	308	587	316	601
80	283	541	297	567	315	599	334	633			366	690	319	607	349	660
90	296	565	303	577											392	737
95																
Max Vol	90	90	92	92	88	88	82	82	79	79	80	80	89	89	NA	NA
Max Temp	296	565	303	577	318	604	335	635	350	662	366	690	339	643	440	824

[a]Data obtained from various references as listed below. NA means not available.

No. 1-5: EMRC 2nd qtrly Table 2.2, 2nd qtrly Table 2.1, 1st qtrly Table 1, Data pack Table 8, Data pack Table 10 respectively.
No. 6: ANG Memorandum, 1/26/87, Tar Oil typical analysis.
No. 7-8: WRI qtrly on 3/11/87, Table 1.

TABLE 16

TAR OIL, ASTM D86 DISTILLATE FRACTIONS

SPECIFIC GRAVITY, 1.075:

VOL. %	TEMPERATURE °F	TEMPERATURE °C	WT% OF FRAC.	WT% C	WT% H	WT% N	WT% O+S (diff)	SUM
IBP	180	82						
5%	275	135	4.49	86.69	10.33	0.56	2.42	100
10%	347	175	4.59	81.62	9.66	0.87	7.85	100
20%	381	194	9.07	80.38	9.59	0.78	9.25	100
30%	405	207	9.37	79.63	9.19	0.67	10.51	100
40%	430	221	9.56	80.88	8.76	0.81	9.55	100
50%	473	245	9.46	83.04	8.86	0.87	7.23	100
60%	511	266	9.27	83.74	8.96	0.85	6.45	100
70%	511	266	9.95	84.64	8.78	0.63	5.95	100
80%	541	283	9.76	85.33	8.91	0.67	5.09	100
90%	565max	296	10.44	85.32	9.13	0.65	4.90	100
RESIDUE			10.54	90.11	4.90	1.15	3.84	
TOTAL WT%			96.50	80.90	8.36	0.75	6.49	
ORIGINAL SAMPLE WT%			100.0	82.60	8.63	1.01	7.76	
RECOVERY %			96.5	97.9	96.9	74.4	83.6	

Thermal Stability During D86 Distillation

Distillation of the tar oil stream, especially as the heavier ends are approached, will not be straight forward and will require vacuum if a deep cut is desired. The main problem is that the heavy ends are thermally unstable and, depending on the heat input rates (i.e., distillation rate), tend to polymerize into nondistillable residue. In tests where the distillation was at recommended D86 rates (3 to 3.5 ml/min), the residue was 30% or greater. The amount of residue produced in the ASTM D86 distillation varied depending on the heating rates to 10 vol% over, and the subsequent heating rates. In no cases were we able to reach the heating rates (ambient to IBP in 10 to 15 min) or distillation rates (4 to 5 ml/min) with this material which were desired. However, in cases for slow heating to IBP and distillation rates of 1 to 2 ml/min, distillation residues as low as 11% were achieved. Decomposition (i.e. smoking) was observed at temperatures as low as 280°C which led to difficulties in assessing the end point. The relationship between the overhead and pot temperatures are depicted in Figure 11.

The stability of the tar oil was investigated by performing the distillation at different heating rates. In order to determine the trends in the final distillate volume associated with the distillation rates, various plots were made of the tar oil D86 distillation data. An overall plot of temperature versus time for the various D86 tests indicated that a correlation may exist between the initial rate of temperature change (between time = 0 and when 10 vol% had distilled) and the final volume of distillate that was collected. Plots of the heating rate between time = 0 to IBP, IBP to 5% distillate, 5 to 10%, and the other combinations versus the total distillate recovered all gave the same trends. Figure 12 depicts the least squares values of the heating rates between time = 0 and 10 vol% over for the various tests against the total volume percent recovered. At heating rates of over 2°C/min recoveries were depressed. The best recovery of 92% was obtained with a constant 2.5°C/min throughout the distillation. Other tests had various initial and later heating rates which may have improved or depressed recoveries.

Faster heating rates generally showed an increase in the amount of non-distillables and varied final temperatures. Molecular weight distributions of the THF solubles of non-distillables were determined by gel permeation chromatography (GPC). GPC analysis showed a larger amount of lower molecular weight material present in residues that reached a lower final temperature. This can be seen in Figure 13. This indicates that the decomposition point of the tar oil shifts when different heating rates are applied.

A cold charge autoclave run was also made to test the stability of the tar oil. The tar oil was heated to 260°C and

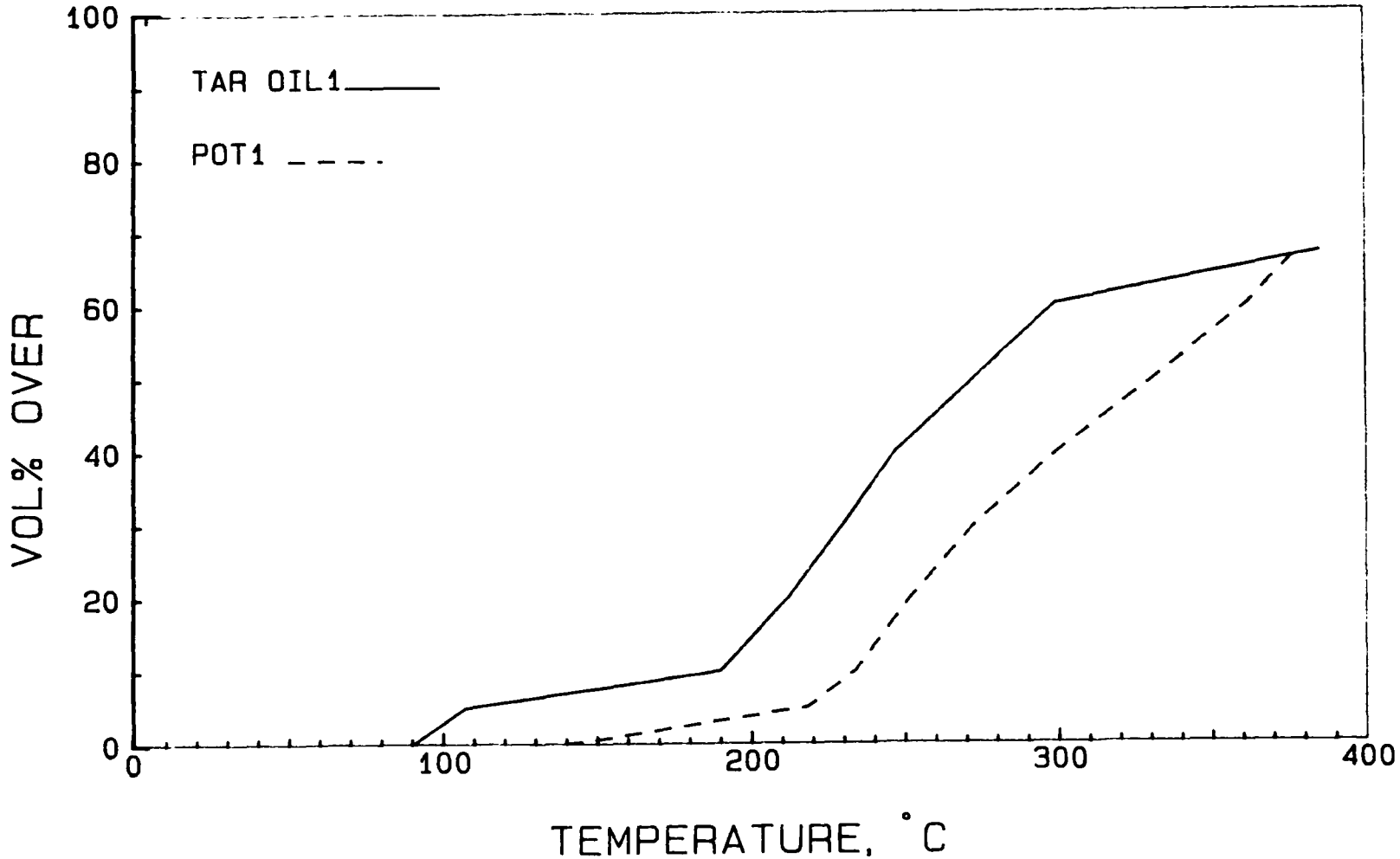


Figure 11. D86 distillation of tar oil comparing pot temperature to overhead temperature.

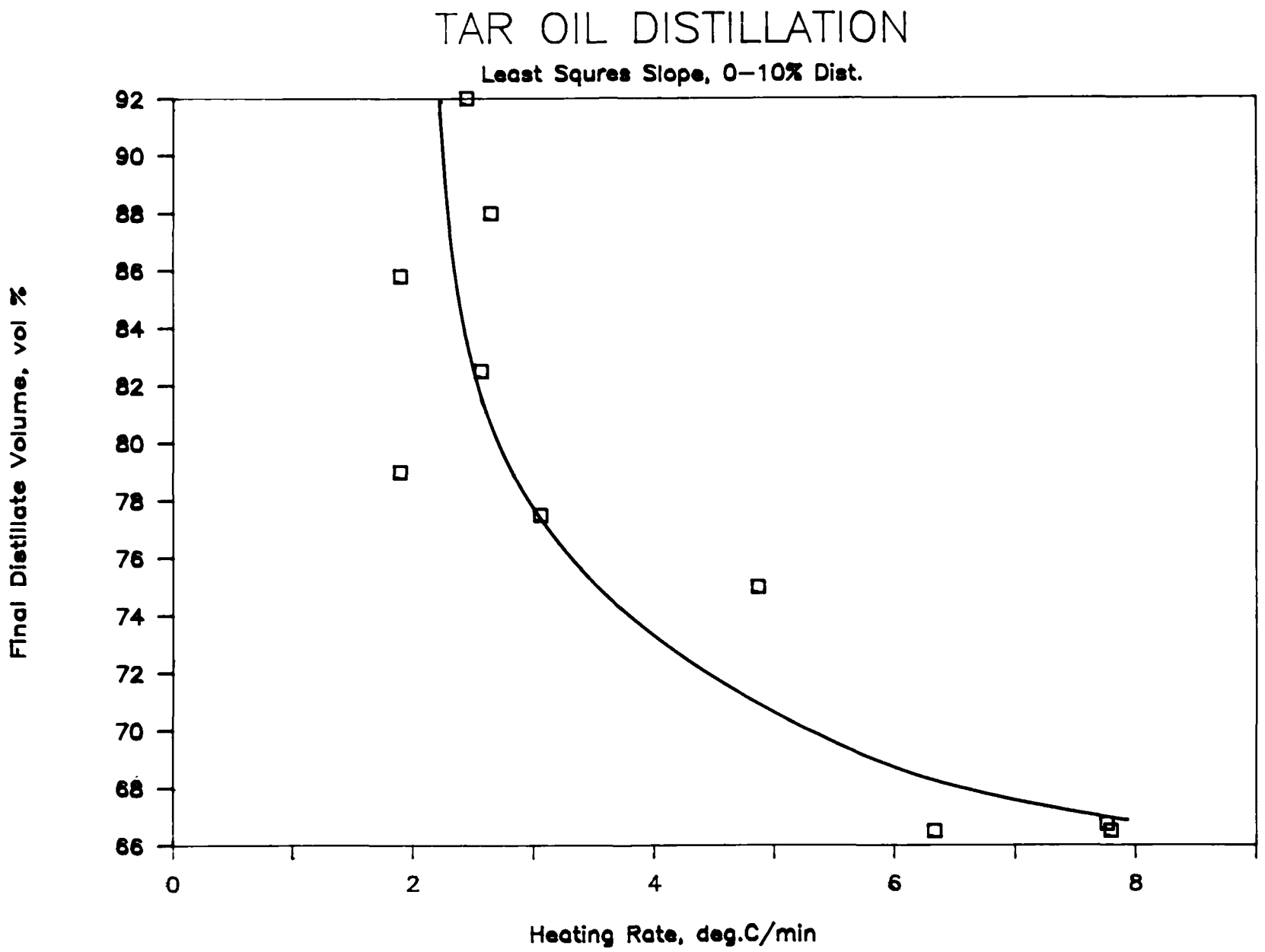


Figure 12. Relationship of initial heating rate to final distillate volume.

held at temperature for 2 hours, then allowed to cool to room temperature. The autoclave was sampled at various times during the run and the samples were analyzed to determine molecular weight changes. GPC analysis showed little polymerization taking place at this temperature. Figure 14 shows the molecular weight distributions of the original tar oil and that of the tar oil after completion of the run. This indicates that little polymerization took place at this temperature. Stability testing at higher temperatures would be required to observe molecular weight changes.

Component Analysis

GC and GC-MS analysis can provide detailed data concerning components in complex mixtures. Figure 15 depicts the GC-FID output for the tar oil stream while Table 17 provides detailed information. The tar oil stream contains about 13 area% phenolics (summed from Table 17). About 13 area% of light boiling toluene and xylenes are present. Aromatic naphthalene and substituted naphthalenes (22 area%) as well phenanthrenes (or anthracenes) (4 area%) are well represented. Small quantities of other aromatics such as biphenyl, acenaphthene, fluorene, and even pyrene are present. Oxygen in this stream is also found in various benzofuran structures. A series of various aliphatics is also present. Nitrogen compounds have been concentrated by acid extraction and are discussed elsewhere. Area% only are reported since not all species were identified.

Aliphatics, Aromatics and Polar Content

The tar oil stream has been separated into aliphatics, aromatics, and polars by solvent elution from a silica gel column. Short-column chromatography separation involves the eluting of aliphatics with pentane and isooctane, aromatics with methylene chloride, and polars with methanol from a highly activated silica gel column on which the total sample had been adsorbed. Elemental, NMR, and GC/MS analyses of the fractions provides additional information about this stream.

Yield, Recovery, and Elemental Data

The tar oil is the most complex stream containing aliphatics (7.9 wt%), aromatics (47.7 wt%) and polars (35.7 wt%). Table 18 presents yield data and the elemental data for the total tar oil sample and for the column fractions. The overall recovery was

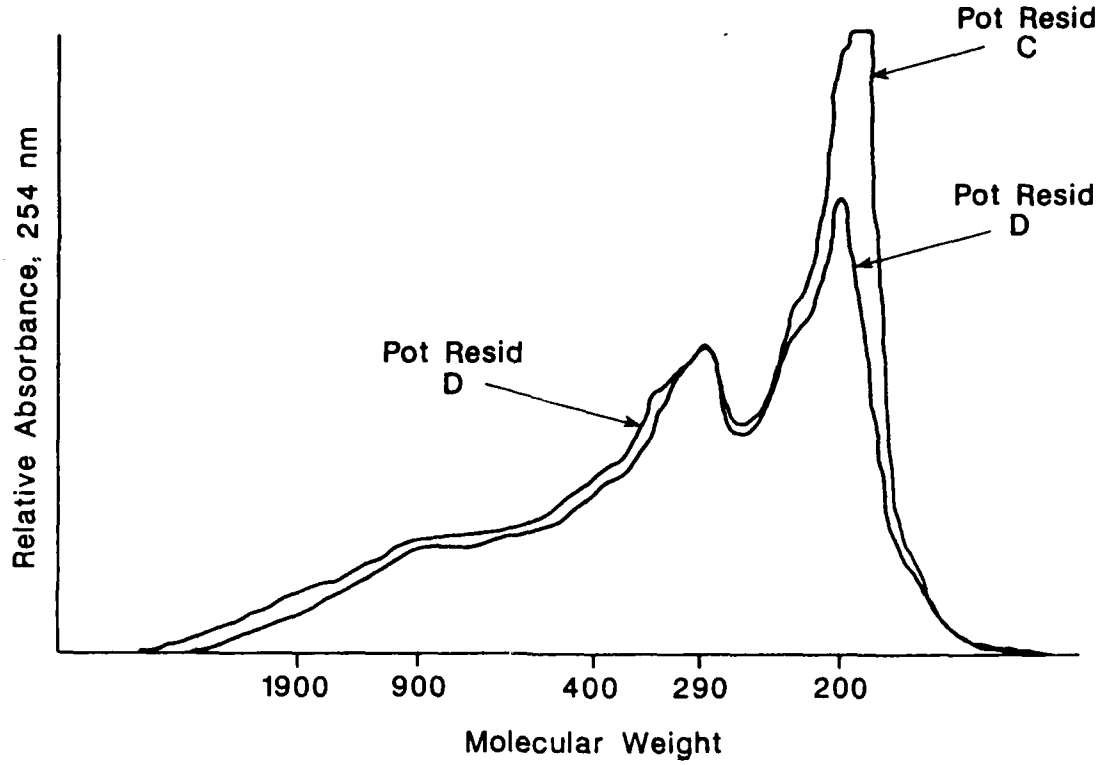


Figure 13. Molecular weight distributions of ASTM D-86 distillation pot residues of tar oil. Pot resid C: 36.44% residue, final temp. 305°C, 0% THF insoluble. Pot resid D: 23.96% residue, final temp 318°C, 0.24% THF insoluble.

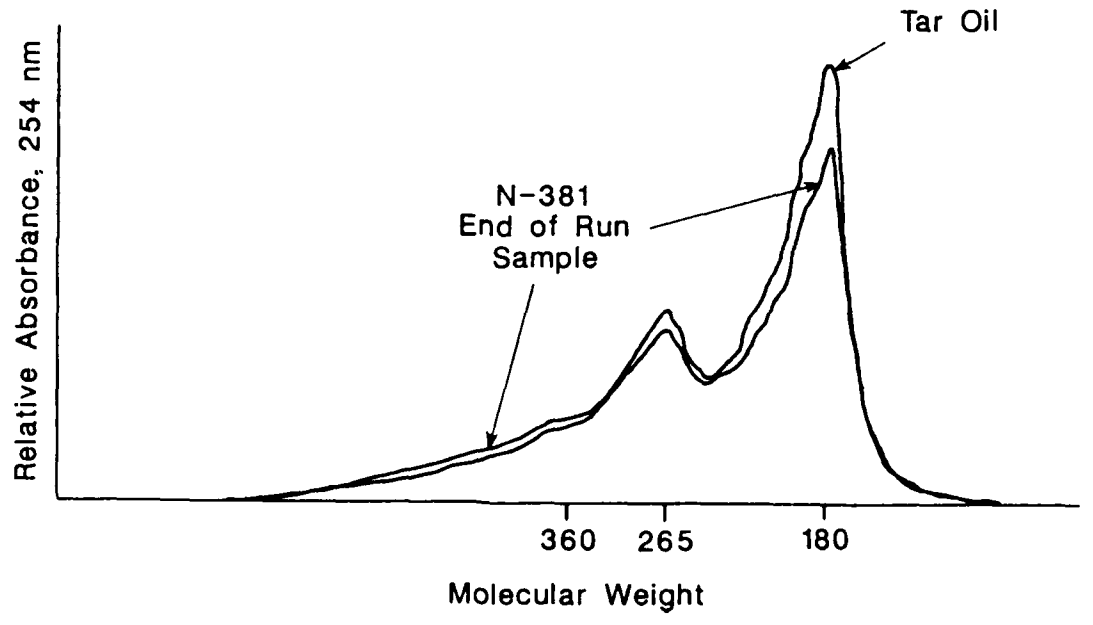


Figure 14. Molecular weight distributions of tar oil before and after autoclave stability test.

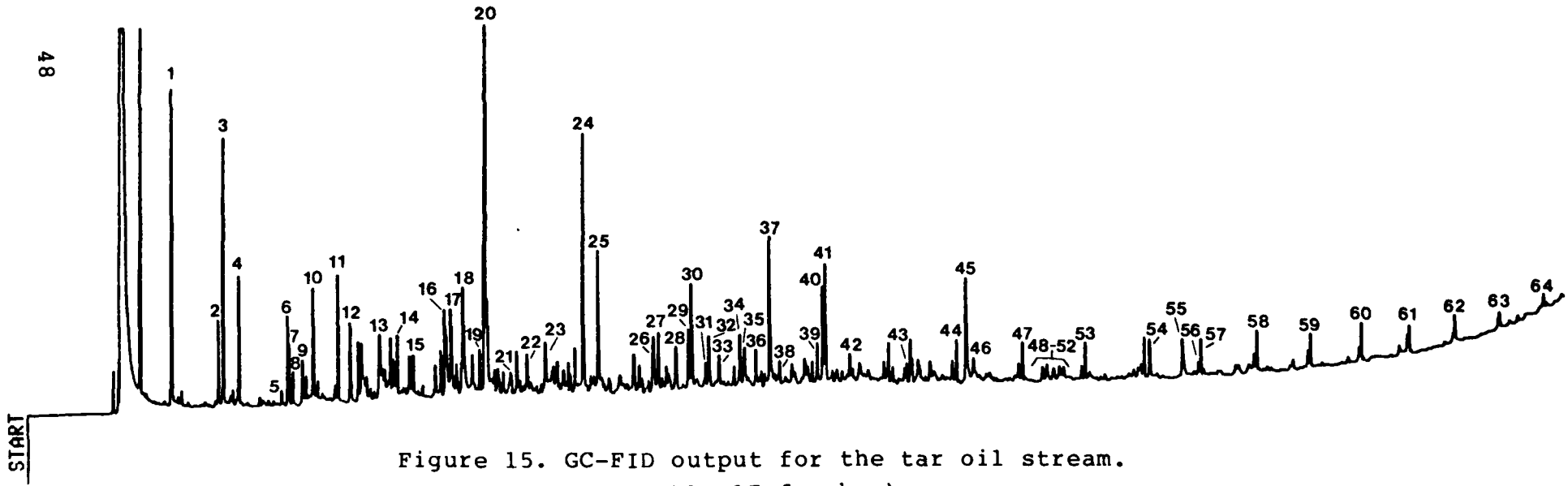


Figure 15. GC-FID output for the tar oil stream.
(see Table 17 for key)

TABLE 17

TAR OIL COMPONENT DATA

GC #	b.p. °C	b.p. °F	Component	Area% Over	Retention Index	Peak Area%	Elemental, atomic C	H	N	O	S
1	111	231	Toluene	8	3.22	8.34	7	8			
2	138	281	C2 Benzene	9	5.40	0.70	8	10			
3	139	282	C2 Benzene	12	5.52	2.56	8	10			
4	144	292	C2 Benzene	13	5.96	1.39	8	10			
5			C3 Benzene	13	7.16	0.18	9	12			
6			C3 Benzene	14	7.33	0.86	9	12			
7	182	359	Phenol	15	7.36	0.66	6	6		1	
8			C3 Benzene	15	7.48	0.32	9	12			
9			C3 Benzene	16	7.75	0.62	9	12			
10			C4 Benzene	17	8.06	1.44	10	14			
11	191	376	C1 Phenol	18	8.76	1.30	7	8		1	
12	202	396	C1 Phenol	19	9.10	1.10	7	8		1	
13			C2 Phenol	21	9.94	1.65	8	10		1	
14			C1 Benzofuran	22	10.78	0.76	9	8		1	
15			C2 Phenol	22	10.88	0.55	8	10		1	
16			C2 Phenol	24	11.77	1.09	8	10		1	
17			C2 Phenol	25	11.94	1.76	8	10		1	
18			C2 Phenol	28	12.28	2.29	8	10		1	
19			C2 Phenol	28	12.54	0.85	8	10		1	
20	218	424	Naphthalene	37	12.88	8.54	10	8			
21			C2 Benzofuran	37	13.38	0.37	10	10		1	
22			C3 Phenol	38	13.75	0.79	9	12		1	
23			C3 Phenol	39	14.56	1.22	9	12		1	
24	240	464	2-Methylnapth.	43	15.62	3.59	11	10			
25	241	466	1-Methylnapth.	45	16.06	1.84	11	10			
26	256	493	Biphenyl	46	17.08	0.90	12	10			
27	254	489	C14H30	47	17.63	1.37	14	30			
28			C2 Naphthalene	48	18.26	0.96	12	12			
29			C2 Naphthalene	49	18.61	1.02	12	12			
30			C2 Naphthalene	50	18.69	1.42	12	12			
31			C2 Naphthalene	51	19.08	0.47	12	12			
32			C2 Naphthalene	52	19.17	0.97	12	12			
33			C2 Naphthalene	52	19.45	0.35	12	12			
34	271	519	C15H32	53	20.02	0.93	15	32			
35	279	534	Acenaphthene	54	20.15	0.95	12	10			
36			C3 Naphthalene	55	20.47	0.66	13	14			
37	287	549	Dibenzofuran	57	20.85	2.00	12	8		1	
38			C3 Naphthalene	57	21.11	0.45	13	14			
39	287	549	C16H34	58	22.17	0.44	16	34			
40	294	561	Fluorene	59	22.32	1.44	13	10			
41			C3 Naphthalene	61	22.40	1.63	13	14			
42			C1 Dibenzofuran	61	23.10	0.47	13	10			

TABLE 17 (cont.)

TAR OIL COMPONENT DATA

GC #	b.p. °C	b.p. °F	Component	Area% Over	Retention Index	Peak Area%	Elemental, atomic C	H	N	O	S
43			C1 Fluorene	61	24.73	0.29	14	12			
44	316	601	C18H38	62	26.15	0.64	18	38			
45	340	644	Phenanthrene	64	26.42	2.33	14	10			
46	340	644	Anthracene	65	26.62	0.55	14	10			
47	330	625	C19H40	65	28.00	0.47	19	40			
48			C1 Phenanthrene	65			15	12			
49			C1 Phenanthrene	66	28.56	0.28	15	12			
50			C1 Phenanthrene	66	28.69	0.43	15	12			
51			C1 Phenanthrene	66			15	12			
52			C1 Phenanthrene	67	29.04	0.35	15	12			
53	343	649	C20H42	67	29.77	0.46	20	42			
54	357	674	C21H44	68	31.61	0.63	21	44			
55	375	707	Fluoranthene	69	32.55	1.08	16	10			
56	369	695	C22H46	69	33.07	0.52	22	46			
57	393	739	Pyrene	69			16	10			
58	380	716	C12H48	70	34.63	0.55	23	48			
59	391	736	C24H50	70	36.11	0.45	24	50			
60	402	755	C25H52	71	37.55	0.48	25	52			
61	412	774	C26H54	71	38.93	0.33	26	54			
62	442	828	C27H56	72	40.26	0.61	27	56			
63	432	809	C28H58	72	41.54	0.35	28	58			
64	441	825	C29H60	72	42.78	0.01	29	60			

TABLE 18

ELEMENTAL ANALYSIS OF TAR OIL TOTAL AND COLUMN FRACTIONS

Crude Phenols	Fraction wt%	Elemental Composition, wt% C	H	N	S	O+S[a]	KF-water[b]
Total, AR[c]	100.0	83.76	8.83	0.52	0.39	6.89	1.20
, mf[d]	98.8	84.78	8.80	0.53	0.39	5.89	.
Aliphatics	7.9	85.24	14.66	0.11	NA	0.00	NA
Aromatics	47.7	88.82	8.36	0.20	NA	2.62	NA
Polars	35.7	75.46	7.62	0.85	NA	16.07	NA
Recovery	92.5[e]	89.7	89.4	77.4		118.5	

[a] Oxygen by difference, NA means not analyzed.
[b] Karl-Fisher Analysis in wt% of total sample.
[c] As received.
[d] Moisture free.
[e] Water is not recovered from the column, but has been included in the recovery calculation.

92.4% of the moisture free (mf) organics charged. Water and some organics are irreversibly adsorbed to silica gel and lighter organics are lost during the removal of eluting solvent under vacuum by rotary evaporation. Carbon and hydrogen recoveries were similar, 89%, and the error is magnified in the oxygen by difference value. Nitrogen values have not been corrected for a high blank value of 0.1 to 0.2 wt%. However, the high nitrogen content in the polars was expected since many nitrogen compounds are highly polar. The high oxygen content in polars is due to the presence of phenolics while in the aromatic fraction the oxygen content is due to dibenzofurans. The aliphatic fraction contains the highest hydrogen content but is also the smallest fraction.

Hydrogen Distribution

Figure 16 depicts the NMR data for the total tar oil samples and the aliphatic, aromatic, and polar fractions. Note that the aliphatic fraction is essentially void of aromatics indicating that a good separation was obtained. The polar fraction contains aromatic protons (5.9-9 ppm region) and most are associated with phenolics. The aromatic regions of the tar oil stream indicate multiple ring aromatics are present.

Table 19 presents the proton distribution data for hydrogen in different structural units as a percentage of the total hydrogen observed and also shows that recoveries (or mass balances) are satisfactory (data from Table 18 was used in the calculations). The aliphatic fraction exhibits high H-aliphatic and H in methyl ($-CH_3$) values. In the aromatic fraction, the presence of alkyl-aromatic groups is shown by the high H-alpha value of 32.1 and that the average chain length of the alkyl groups is of moderate length is shown by the lower H in $-CH_3$ value. The H-Beta value of 5.6% indicates the potential presence of tetralin-like hydrogenated aromatics. The hydrocarbon portions of the molecular structure of the polar fraction contain mainly aromatics with methyl side chains.

TABLE 19

HYDROGEN DISTRIBUTION NMR ANALYSIS OF TAR OIL COLUMN FRACTIONS

Range (ppm)	Hydrogen Type	Total Sample (wt%)	Aliphatic (wt%)	Aromatic (wt%)	Polar (wt%)	Percent Recovery
9.0-5.9	Aromatic	28.3	1.8	27.6	40.0	99.2
4.4-3.5	Fluoranthene	2.4	0.2	3.2	0.0	68.8
3.5-3.3	Acenapthene	0.5	0.1	1.1	0.0	114.4
3.3-1.9	H-Alpha	28.4	1.7	32.1	35.1	100.9
1.9-1.5	H-Beta	5.3	4.2	5.6	4.6	95.2
1.5-1.0	H-Aliphatic	23.4	64.2	17.8	14.3	100.1
1.0-.06	H in $-CH_3$	11.7	27.8	12.6	6.0	107.3
		100.0	100.0	100.0	100.0	100.0
Normalized Wt% of Fraction		100.0	8.7	52.2	39.1	100.0
Normalized Wt% of H in Fraction		8.83	15.02	8.57	7.80	100.0

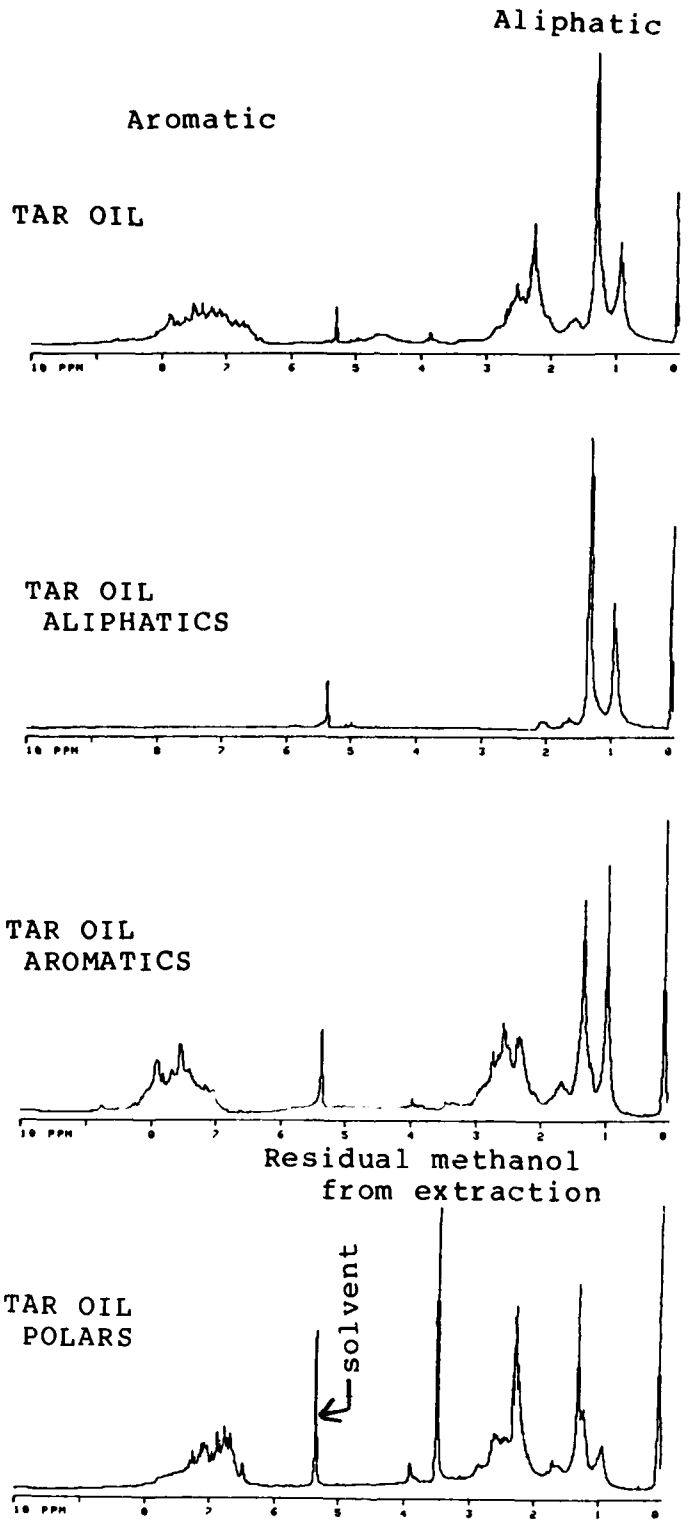


Figure 16. Tar oil proton NMR spectrum of each short column fraction.

Component and Volatility Comparisons

Figure 17 depicts the difference between the total tar oil sample and the aromatic and polar fractions using GC data. The vertical axis is in cumulative area% of sequentially eluting compounds from a GC column. The horizontal axis is the eluting temperature of the compound. As will be seen, the use of these profiles provides more detail in that compounds that are higher in concentration are readily noticed. The compounds were identified by MS and often more than one isomer or compound with the same elemental composition were present.

In Figure 17 for the polar fraction (36 wt%) the compounds causing the area% increases at about 190°C are C1-phenols (5 and 12 area%). C2-phenols are present at 210°C. Various alkylated naphthols are present around 270°C. In general most of the polar fraction consists of the various isomers of alkylated phenols and naphthols. Small amounts of methoxyphenols are also present.

The aromatic fraction (48 wt%) shows the highest concentration of naphthalene (8 area%) and alkylated naphthalenes. Smaller amounts of indans and indenes are present. Three ring aromatics such as fluorene (2 area%), phenanthrene (3 area%), pyrene (2 area%) and their alkylated derivatives elute from the GC column at higher temperatures. Dibenzofuran (3 area%), and its alkylated derivatives are the major oxygenated compounds in the aromatic fraction. In comparison to the total tar oil sample, the polars are found more at lower temperatures while the aromatics are found in the higher temperature regions.

Figure 18 compares the tar oil to the aliphatic fraction (8 wt%). The step increases caused by normal alkanes from C11 at 196°C to C24 at 391°C are readily apparent. Lower boiling alkanes would probably be lost during vacuum evaporation to remove pentane solvent and would be lost during the removal of octane solvent. Higher boiling normal alkanes up to C30 were present in this fraction. The low concentration of the aliphatic fraction in the tar oil obscures observing the alkane steps in the GC area% profile.

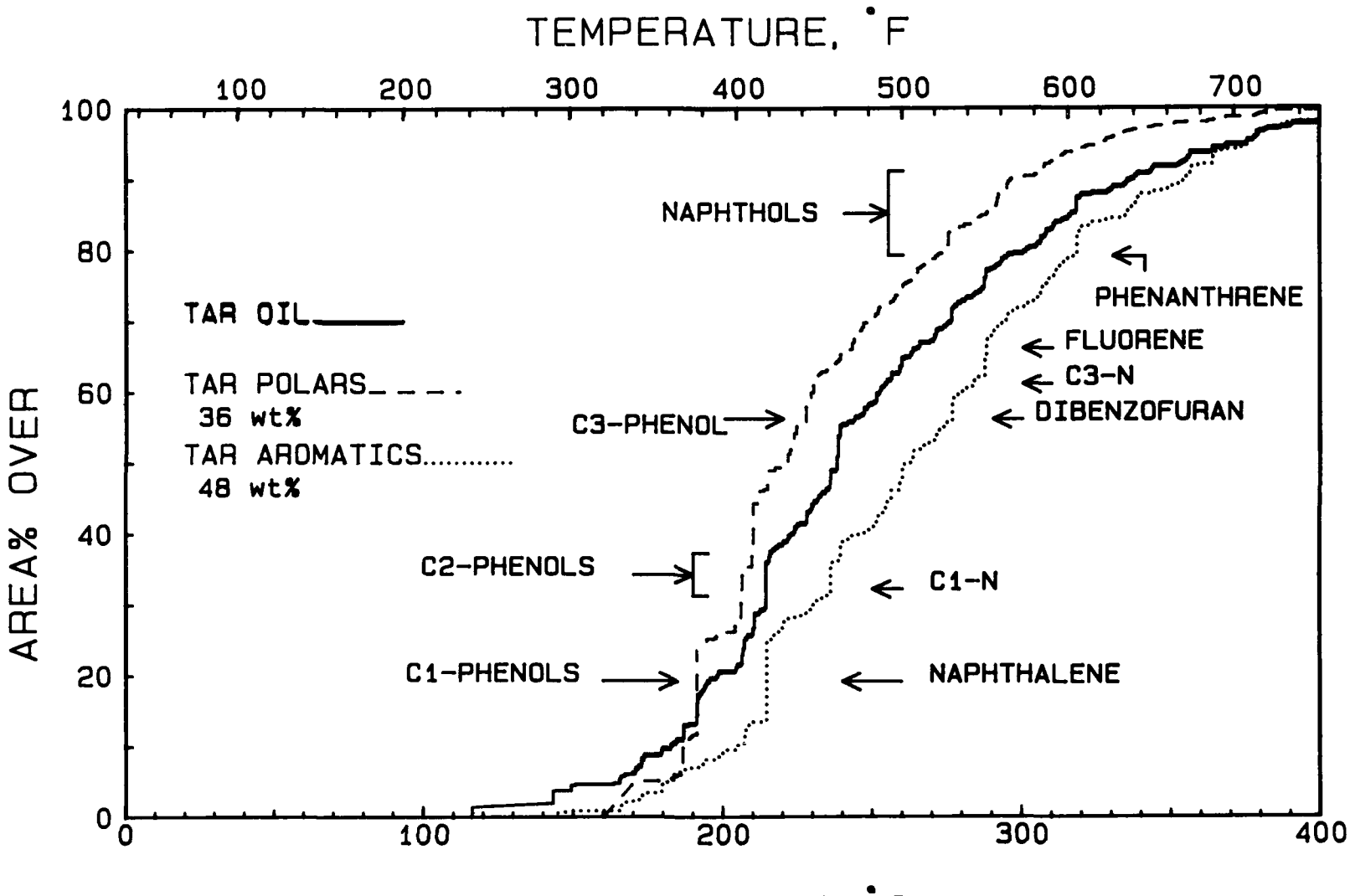


Figure 17. Cumulative GC area% vs. temperature in °C(°F) for tar oil, tar oil polar, and tar oil aromatic fractions.

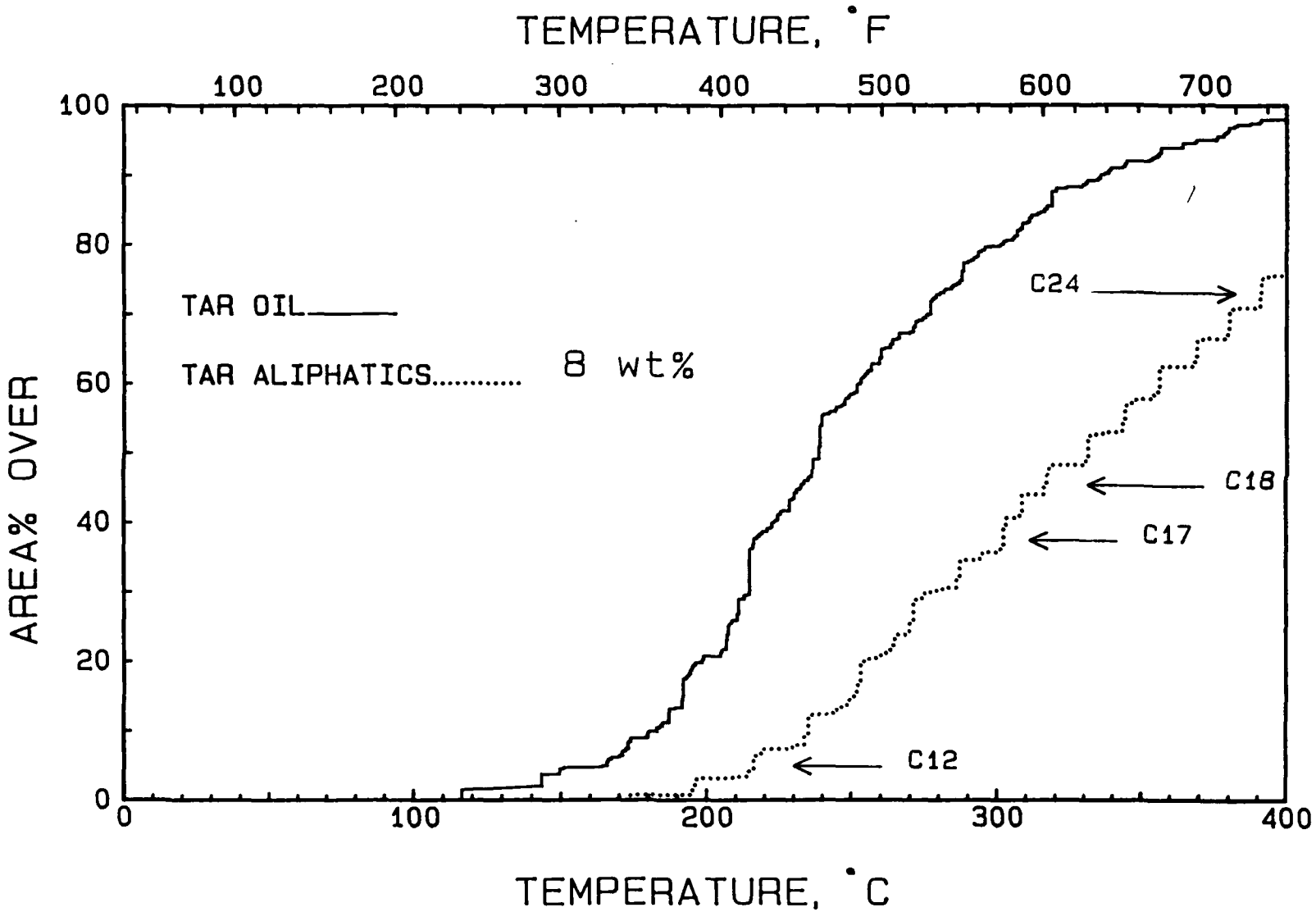


Figure 18. Cumulative GC area% vs. temperature in °C(°F) for tar oil and tar oil aliphatic fractions.

Acid, Base, and Neutral Fractions

Acid (28 wt%), base (2.5 wt%), and neutral (48 wt%) fractions were prepared by sequential extraction of a tar oil-pentane solution with aqueous base (NaOH) and aqueous acid (HCl) followed by removal of the pentane under vacuum. The closure was low at 79% due to losses to water phases and during solvent stripping (see experimental). However, the material recovered and analyzed does represent material that is present in the tar oil stream.

Acid and Neutral Fractions

Figure 19 depicts the GC data for comparison to the acid and neutral fractions with each other and with the total tar oil. This figure will essentially superimpose Figure 17 indicating the close similarity of the extraction acid and neutral fractions and column polar and aromatic fractions, respectively. However, the neutral fraction obtained by extraction does contain normal alkanes which are not present in the aromatic fraction obtained by column separation.

Base Fraction (Nitrogen Bases)

A fraction of major interest is the base fraction which is composed of nitrogen-containing compounds (Figure 20). Quinoline is present in the largest concentration (at 225°C). In general, the nitrogen-containing compounds were found in the higher boiling regions (Figure 20). Table 20 presents detailed component data on the GC-MS analysis of the base fraction. This indicates that most individual compounds are present in small amounts even in this concentrated sample.

Some of the nitrogen containing compounds were identified using GC-FTIR analysis. Aniline (Figure 21) and lutidine (an isomeric dimethylpyridine, Figure 22) were positively identified by their infrared spectra. In addition several nitrogen heterocycles containing a carboxyl functionality have been tentatively identified as related to pyrolidinone. Table 21 presents concentration data in area% of this fraction for pyridine, quinoline, aniline, and their alkylated derivatives.

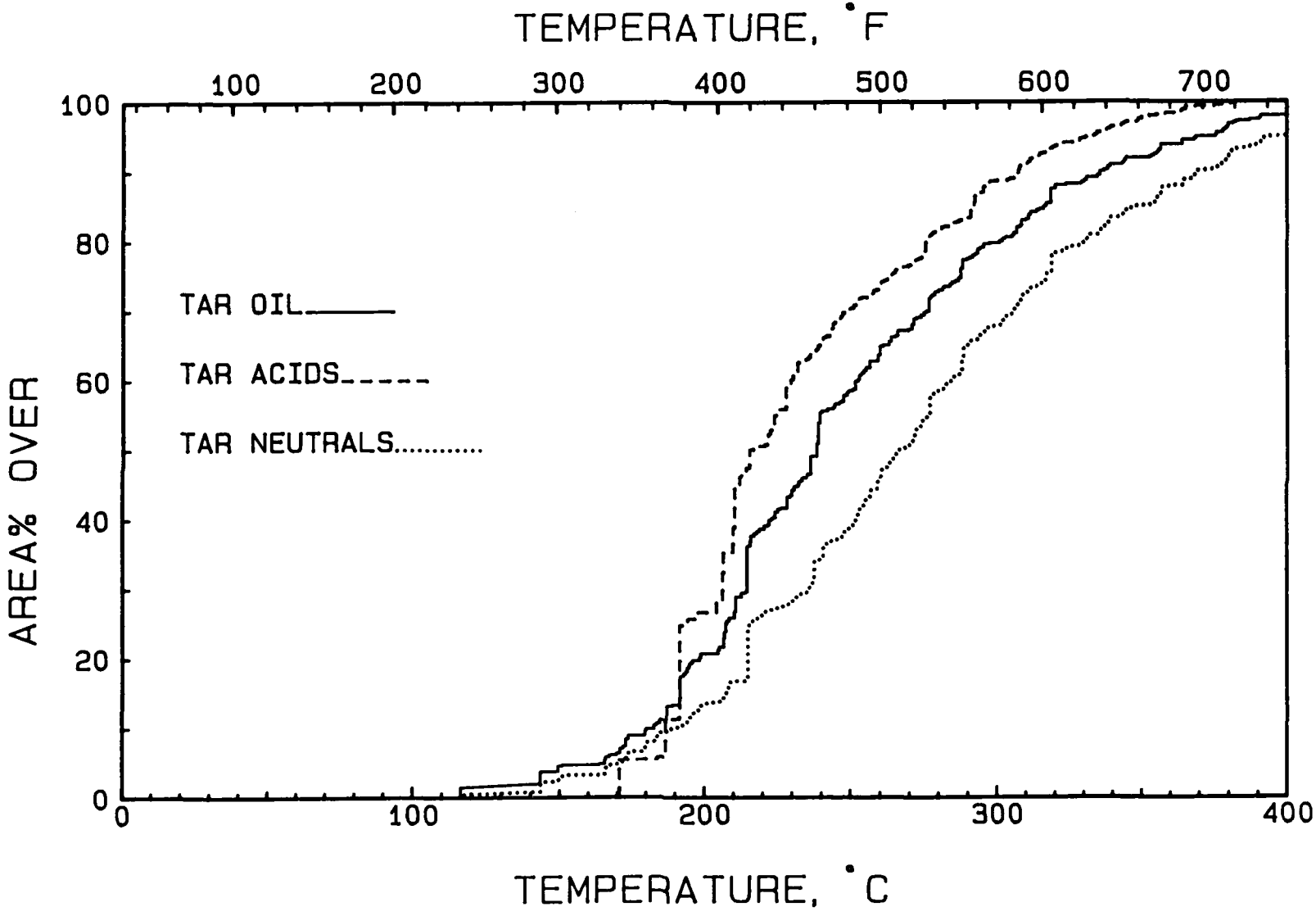


Figure 19. Cumulative GC area% vs. temperature in °C(°F) for tar oil, tar oil acids, and tar oil neutral fractions.

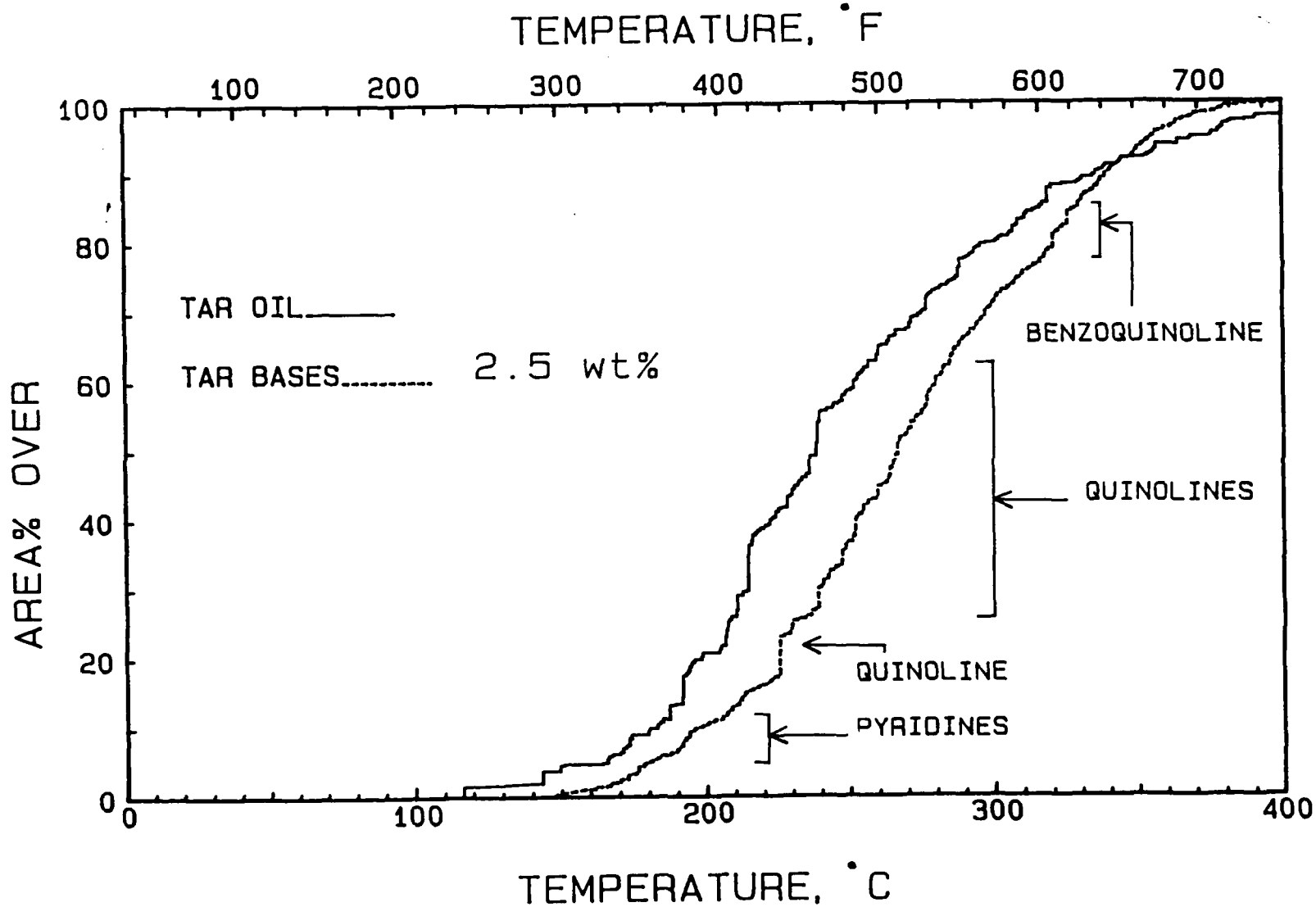


Figure 20. Cumulative GC area% vs. temperature in °C(°F) for tar oil and tar oil base fraction.

TABLE 20

TAR OIL BASES - COMPONENT DATA

GC #	b.p. °C	b.p. °F	Component	Area% Over	Retention Index	Peak Area%	Elemental, atomic C	H	N	O	S
1			C2 Pyridine	0	886	0.28	7	9	1		
2			C2 Pyridine	1	932	0.83	7	9	1		
3			C2 Pyridine	1	947	0.33	7	9	1		
4			C2 Pyridine	2	962	0.15	7	9	1		
5			C2 Pyridine	2	967	0.44	7	9	1		
6			C1 Pyridine	2	981	0.08	6	7	1		
7	184	363	Aniline	3	983	0.42	6	7	1		
8			C3 Pyridine	3	994	0.58	8	11	1		
9			C3 Pyridine	3	998	0.20	8	11	1		
10			C2 Pyridine	4	1006	0.28	7	9	1		
11			C3 Pyridine	4	1010	0.73	8	11	1		
12			C3 Pyridine	5	1018	0.23	8	11	1		
13			C3 Pyridine	5	1020	0.22	8	11	1		
14			C3 Pyridine	5	1026	0.15	8	11	1		
15			C3 Pyridine	5	1028	0.16	8	11	1		
16			C3 Pyridine	5	1031	0.29	8	11	1		
17			C3 Pyridine	6	1038	0.15	8	11	1		
18				6	1045	0.39					
19			C1 Aniline	6	1054	0.16	7	9	1		
20			C3 Pyridine	6	1061	0.27	8	11	1		
21			C4 Pyridine	6	1068	0.12	9	13	1		
22			C3 Pyridine	7	1071	0.32	8	11	1		
23			C4 Pyridine	7	1073	0.36	9	13	1		
24			C2 Aniline	7	1076	0.11	8	11	1		
25			C1 Aniline	8	1079	0.90	7	9	1		
26			C1 Aniline	8	1085	0.31	7	9	1		
27			C4 Pyridine	9	1091	0.87	9	13	1		
28			C4 Pyridine	10	1094	0.18	9	13	1		
29			C4 Pyridine	10	1098	0.32	9	13	1		
30			C2 Aniline	10	1102	0.10	8	11	1		
31			C4 Pyridine	10	1107	0.07	9	13	1		
32			C4 Pyridine	10	1111	0.13	9	13	1		
33			C4 Pyridine	10	1113	0.09	9	13	1		
34				10	1114	0.08					
35	229	444	Dihydroindole	11	1120	0.20	8	9	1		
36			C4 Pyridine	11	1123	0.14	9	13	1		
37			C5 Pyridine	11	1131	0.24	10	15	1		
38			C4 Pyridine	11	1134	0.14	9	13	1		
39			C5 Pyridine	12	1147	0.56	10	15	1		
40				12	1155	0.38					
41				12	1157	0.32					
42			C5 Pyridine	12	1161	0.08	10	15	1		
43			C2 Aniline	13	1164	0.39	8	11	1		
44				13	1166	0.18					
45				13	1171	0.15					

TABLE 20 CONTINUED

GC #	b.p. °C	b.p. °F	Component	Area% Over	Retention Index	Peak Area%	Elemental, atomic C	H	N	O	S
46			C2 Aniline	13	1175	0.36	8	11	1		
47				14	1178	0.25					
48			C2 Aniline	14	1181	0.43	8	11	1		
49				14	1184	0.16					
50	251	484	Tetrahydro-quino	15	1186	0.53	9	11	1		
51				15	1190	0.09					
52				15	1194	0.21					
53	218	424	Naphthalene	15	1199	0.12	10	8	1		
54				15	1208	0.21					
55				16	1210	0.21					
56				16	1213	0.09					
57			C5 Pyridine	16	1216	0.15	10	15	1		
58			C5 Pyridine	16	1219	0.12	10	15	1		
59			C5 Pyridine	16	1225	0.13	10	15	1		
60				16	1227	0.13					
61				16	1231	0.19					
62	251	484	Tetrahydro-quino	17	1234	0.44	9	11	1		
63				17	1240	0.17					
64				17	1246	0.10					
65	238	460	Quinoline	23	1251	5.68	9	7	1		
66			C5 Pyridine	23	1258	0.31	10	15	1		
67				23	1270	0.24					
68	243	469	Isoquinoline	25	1273	1.70	9	7	1		
69				25	1280	0.08					
70				25	1288	0.24					
71				26	1296	0.14					
72				26	1298	0.21					
73				26	1315	0.16					
74				26	1317	0.14					
75			C1 Quinoline	29	1322	2.97	10	9	1		
76				29	1327	0.09					
77			C1 Quinoline	30	1332	0.96	10	9	1		
78				30	1338	0.08					
79				30	1340	0.15					
80			C1 Quinoline	31	1342	0.84	10	9	1		
81				32	1345	0.35					
82				32	1353	0.15					
83			C1 Quinoline	32	1356	0.41	10	9	1		
84				32	1361	0.09					
85				32	1362	0.17					
86			C1 Quinoline	35	1368	2.21	10	9	1		
87			C1 Quinoline	35	1374	0.92	10	9	1		
88				36	1379	0.17					
89				36	1387	0.13					
90			C1 Quinoline	36	1389	0.55	10	9	1		

TABLE 20 CONTINUED

GC #	b.p. °C	b.p. °F	Component	Area% Over	Retention Index	Peak Area%	Elemental, atomic C	H	N	O	S
91			C2 Quinoline	37	1392	0.90	11	11	1		
92			C1 Quinoline	39	1394	1.62	10	9	1		
93				39	1397	0.57					
94				40	1401	0.18					
95			C1 Quinoline	40	1406	0.45	10	9	1		
96			C2 Quinoline	41	1410	0.83	11	11	1		
97				41	1417	0.18					
98			C2 Quinoline	42	1419	0.60	11	11	1		
99				42	1426	0.08					
100				42	1435	0.12					
101			C2 Quinoline	44	1437	1.72	11	11	1		
102			C2 Quinoline	44	1444	0.39	11	11	1		
103				44	1453	0.11					
104				44	1455	0.32					
105			C2 Quinoline	45	1459	0.59	11	11	1		
106			C2 Quinoline	46	1461	1.19	11	11	1		
107				47	1464	0.37					
108			C2 Quinoline	47	1469	0.66	11	11	1		
109			C2 Quinoline	48	1471	0.81	11	11	1		
110	270	518	Phenyl Pyridine	50	1475	1.84	11	9	1		
111			C2 Quinoline	51	1479	0.67	11	11	1		
112				51	1486	0.16					
113				51	1489	0.21					
114			C2 Quinoline	51	1492	0.61	11	11	1		
115				52	1497	0.21					
116			C3 Quinoline	53	1501	0.95	12	13	1		
117			C2 Quinoline	53	1510	0.57	11	11	1		
118			C2 Quinoline	54	1513	0.28	11	11	1		
119			C3 Quinoline	54	1524	0.69	12	13	1		
120			C3 Quinoline	54	1528	0.29	12	13	1		
121				55	1532	0.36					
122	295	563	Diphenyl Amine	56	1535	0.76	12	13	1		
123			C3 Quinoline	57	1537	1.15	12	13	1		
124				57	1543	0.26					
125				57	1545	0.40					
126			C3 Quinoline	58	1548	0.21	12	13	1		
127				58	1550	0.18					
128				58	1555	0.38					
129				59		0.72					
130			C3 Quinoline	59	1561	0.24	12	13	1		
131			C3 Quinoline	60	1565	0.36	12	13	1		
132			C3 Quinoline	60	1568	0.82	12	13	1		
133			C3 Quinoline	61	1573	0.36	12	13	1		
134				62		1.09					
135				62		0.36					

TABLE 20 CONTINUED

GC #	b.p. °C	b.p. °F	Component	Area% Over	Retention Index	Peak Area%	Elemental, atomic C	H	N	O	S
136	295	563	Diphenyl Amine	63	1591	0.84	12	11	1		
137				63		0.24					
138				63		0.23					
139				64		0.45					
140				64		0.43					
141				65		0.30					
142				65		0.14					
143				65		0.16					
144				65		0.21					
145				65		0.08					
146				66		0.58					
147				66		0.27					
148				67		0.46					
149				67		0.24					
150				67		0.31					
151				67		0.22					
152				68		0.22					
153				68		0.22					
154			Indeno-pyridine	69	1665	1.08	12	9	1		
155				69		0.15					
156				69		0.45					
157				70		0.20					
158				70		0.52					
159				70		0.28					
160				71		0.44					
161				71		0.50					
162				71		0.13					
163				72		0.38					
164				72		0.10					
165				72		0.27					
166			C1 Aza-fluorene	73	1730	0.62	13	11	1		
167				73		0.12					
168				73		0.23					
169				74		0.32					
170				74		0.14					
171				74		0.35					
172				74		0.19					
173				74		0.26					
174				75		0.30					
175				75		0.23					
176				75		0.30					
177				76		0.48					
178				76		0.20					
179				76		0.42					
180				77		0.52					

TABLE 20 CONTINUED

GC #	b.p. °C	b.p. °F	Component	Area% Over	Retention Index	Peak Area%	Elemental, atomic C	H	N	O	S
181				77		0.13					
182				77		0.17					
183				77		0.21					
184	338	640	Benzo-quinoline	79	1823	1.93	13	9	1		
185				80		0.44					
186	338	640	Benzo-quinoline	80	1832	0.53	13	9	1		
187				81		0.28					
188				81		0.18					
189	338	640	Benzo-quinoline	83	1858	1.97	13	9	1		
190				83		0.28					
191				83		0.26					
192				84		0.91					
193				85		0.64					
194				85		0.37					
195				85		0.25					
196				86		0.19					
197				86	1929	0.52	14	11	1		
198				87	1938	0.39	14	11	1		
199				87	1943	0.38	14	11	1		
200				87	1946	0.39	14	11	1		
201				88	1955	0.30	14	11	1		
202				88	1959	0.47	14	11	1		
203				88		0.29					
204				89		0.31					
205				89		0.32					
206				89	1980	0.24	14	11	1		
207				90		0.34					
208				90		0.17					
209				90		0.17					
210				90		0.31					
211				90		0.20					
212				91		0.23					
213				91		0.25					
214				91	2042	0.40					
215				92		0.40					
216				92		0.16					
217				92		0.32					
218				92		0.29					
219				93		0.14					
220				93		0.18					
221				93		0.28					
222				93		0.22					
223				94		0.62					
224				94		0.23					
225				94		0.27					

TABLE 20 CONTINUED

GC #	b.p. °C	b.p. °F	Component	Area% Over	Retention Index	Peak Area%	Elemental, atomic C	H	N	O	S
226				95		0.16					
227				95		0.38					
228				95		0.10					
229				95		0.39					
230				96		0.15					
231				96		0.17					
232				96		0.14					
233				96		0.12					
234				96		0.13					
235				97	2209	0.37					
236				97		0.12					
237				97		0.11					
238				97	2273	0.25					
239				97		0.14					
240				98	2289	0.39					
241				98		0.09					
242				98		0.14					
243				98		0.08					
244				98		0.34					
245				98		0.11					
246				98		0.12					
247				99		0.16					
248				99		0.10					
249				99		0.10					
250				99		0.15					
251				99		0.13					

TABLE 21

TAR OIL BASES - ISOMER DATA

Component	No. of Isomers	Area Percent
Pyridine	0	0.00
C1 Pyridine	1	0.08
C2 Pyridine	6	2.31
C3 Pyridine	11	3.30
C4 Pyridine	10	2.42
C5 Pyridine	7	1.59
TOTAL	35	9.70
Quinoline	1	5.68
C1 Quinoline	9	10.93
C2 Quinoline	13	8.97
C3 Quinoline	9	5.07
Benzoquinoline	3	4.43
TOTAL	35	35.08
Aniline	1	0.42
C1 Aniline	3	1.37
C2 Aniline	5	1.39
TOTAL	9	3.18

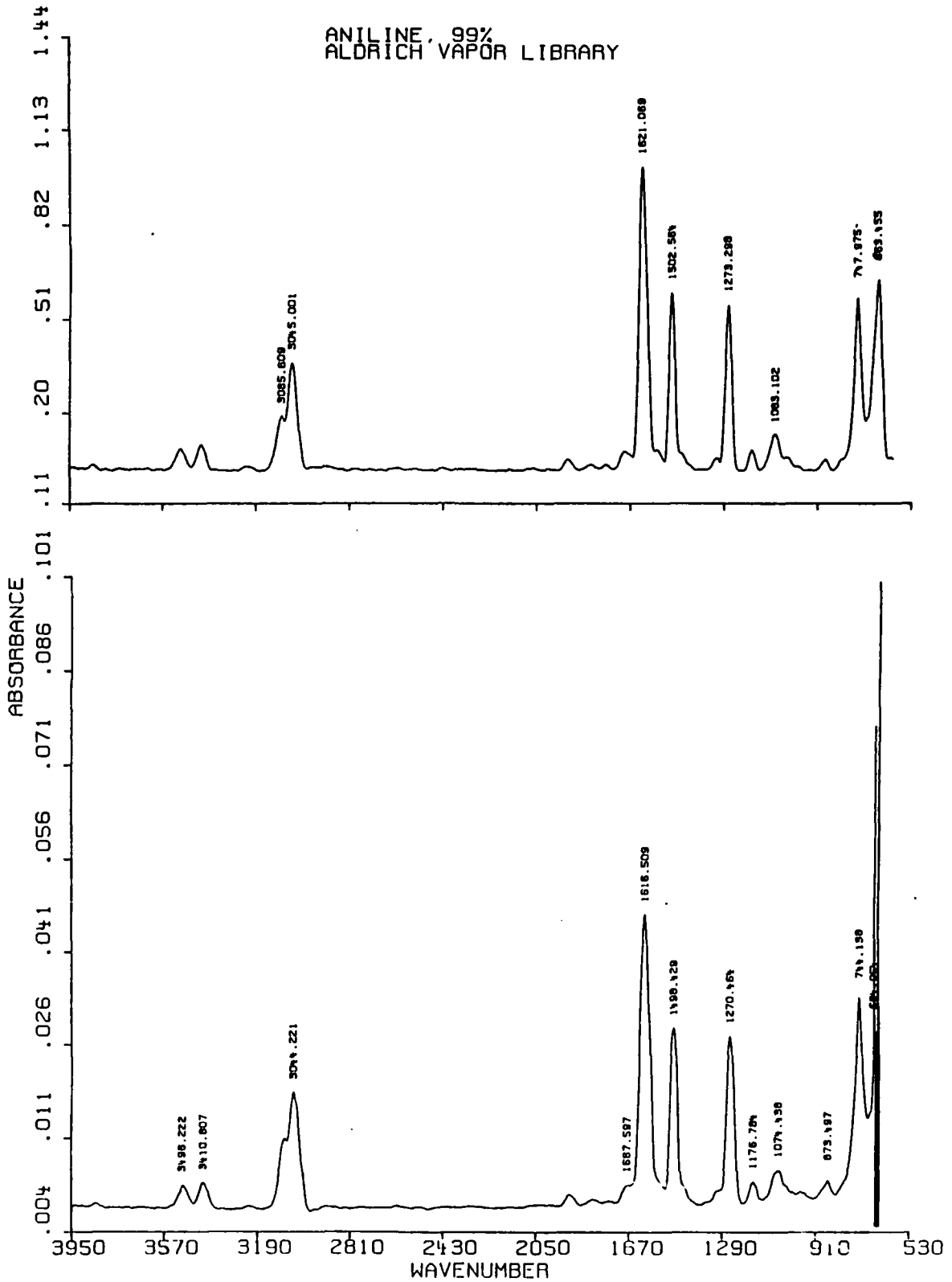


Figure 21. FTIR spectrum of GC peak of aniline from tar oil (bottom) compared to library spectrun (top)

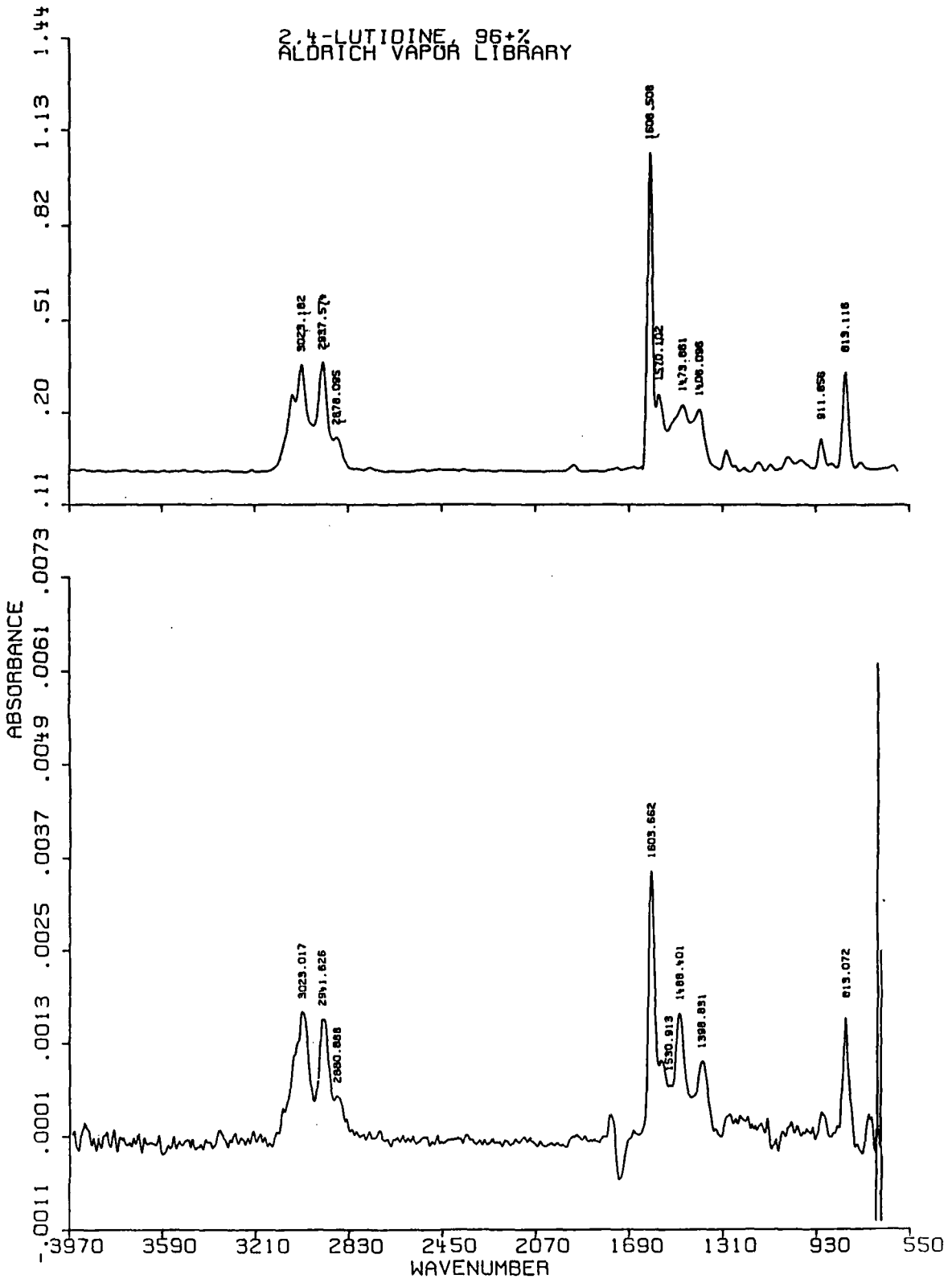


Figure 22. FTIR spectrum of GC peak of lutidine from tar oil (bottom) compared to library spectrum (top)

CRUDE PHENOL STREAM

Elemental Data

Elemental data for the crude phenol stream analyzed by participating labs are presented in Table 22. The ERC and WRI data are from samples provided under this contract while the ANG data is from different samples.

Distillation Data

D86 Distillation Data

The results of various D86 distillation analyses for the crude phenol stream are presented in Table 23.

The collection and analysis of individual D86 distillate fractions add additional information as seen in Table 24. The hydrogen content of the fractions ranges from 7.1 to 7.6 wt% except in the residue where it is only 5.7 wt%. For the phenolic stream the total sulfur content is only 0.04 wt%, so the difference column represents the oxygen level. Oxygen content is 15.2 to 18.5 wt% for all fractions except for the residue which is only 8.9 wt%. The high oxygen content of the initial 5 vol% over is due to the presence of water in this fraction. Nitrogen content is highest in the residue (1.6 wt%).

Component Analysis

GC and GC-MS analysis can provide detailed data concerning components in complex mixtures. Table 25 and Figure 23 provide detailed information on the crude phenol stream. The phenolics (phenol, cresols, and xylenols) account for about 90 area% of the flame ionization detector (FID) output for the crude phenol stream. FID area% values are within about 12% of actual wt% values for components other than phenolics (see Table 6 for response factors). Since numerous dihydroxybenzenes are present in this stream, the calculation of wt% values from area% values would require the use of individual compound response factors. The presence of 1.8 area% of methoxyphenol (potentially guaiacol) and compounds eluting after C2-phenols can be noted. However, the previous data (Table 24) indicated that even the higher boiling material contained 18 wt% oxygen.

TABLE 22

CRUDE PHENOL ELEMENTAL ANALYSIS[a,b]

NO. SAMPLE	1 ERC1		2 ERC2	3 WRI1		4 WRI2		5 ANG1		7 ANG2	
	AR	mf[e]	mf	AR	mf[e]	AR	mf[e]	AR	mf[e]	AR[e]	mf
wt% C	72.18	75.57	76.03	71.30	75.44	71.80	75.49	77.00	80.62	75.59	79.00
H	7.49	7.32	7.34	7.40	7.18	7.20	7.00	6.70	6.49	7.36	7.20
N	0.28	0.29	0.31	0.47	0.50	0.53	0.56	0.40	0.42	0.38	0.40
S	0.04	0.04	NA	0.14	0.15	0.12	0.13	0.10	0.10	0.19	0.20
O[f]	20.01	16.74	16.32	20.69	16.59	20.35	16.71	15.80	12.26	16.29	13.20
total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
water	4.48			5.50		4.90		4.50		4.50	

[a]Data obtained from various references as listed below
[b]AR is as received and mf is moisture free
[e]Calculated values
[f]Oxygen by difference

No. 1-2: EMRC 2nd qtrly Table 2.1 and Table 2.3 respectively.
No. 3-4: WRI qtrly dated 3/11/87, samples 86-73A and 66-73B respectively.
No. 5 : ANG memorandum, 9/16/86
No. 7 : ANG Memorandum, 1/26/87

TABLE 23

CRUDE PHENOL D86 DISTILLATION DATA [a]

NO. SAMPLE	1 ERCP1		2 ERCP2		3 WRIP1		4 WRIP2		5 ANGP1	
Sp Gr	1.060		1.075		1.066		1.066		1.072	
ASTM D86	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F
IBP	97	207	97	207	106	222	155	311	99	210
5	98	208	190	374			183	361		
10	185	365	190	374	153	307	185	365	185	365
20	190	374	194	381	191	376	186	366	193	380
30	193	379	195	383	193	379	186	367	196	385
40	193	379	197	387						
50	196	385	201	394	199	391	191	375	202	395
60	201	394	210	410						
70	210	410	223	433	216	420	199	390	218	425
80	229	444	242	468	244	471	200	392	243	470
90	263	505	258	496			236	457	274	525
95							259	499		
Max Vol	95	95	94	94	92	92			96	96
Max Temp	265	509	258	496	264	507	311	592	299	570

[a]Data obtained from various references as listed below

No.1-2: ERC 2nd qtrly Table 2.1 and Table 2.3 respectively.
No. 3: WRI qtrly, 3/11/87, Table 3 (sample 86-73A)
No. 4: WRI qtrly, 3/11/87, Table 3 (sample 86-73B cal'd from D-2887)
No. 5: ANG memo, 9/16/86

TABLE 24

CRUDE PHENOL D86 DISTILLATE FRACTIONS

SPECIFIC GRAVITY, 1.075:

VOL. %	TEMPERATURE °F	TEMPERATURE °C	WT% OF FRAC.	WT% C	WT% H	WT% N	WT% O+S (diff)	SUM
IBP	207	97						
5%	374	190	4.88	73.01	7.47	0.20	19.32	100
10%	374	190	4.87	76.22	7.19	0.00	16.59	100
20%	381	194	9.73	76.78	7.13	0.00	16.09	100
30%	383	195	9.66	76.29	7.10	0.10	16.51	100
40%	387	197	9.64	76.23	7.16	0.17	16.44	100
50%	394	201	9.74	76.57	7.28	0.16	15.99	100
60%	410	210	9.51	77.33	7.38	0.13	15.16	100
70%	433	223	9.73	77.14	7.46	0.19	15.21	100
80%	468	242	9.64	75.31	7.55	0.28	16.86	100
90%	496	258	10.91	73.72	7.55	0.41	18.32	100
94%	496	258	4.22	73.22	7.60	0.72	18.46	100
RESIDUE			6.23	83.78	5.73	1.59	8.90	100
TOTAL WT%			98.76	75.39	7.15	0.28	15.93	
ORIGINAL SAMPLE WT%			100.0	76.03	7.34	0.31	16.32	
RECOVERY %			98.8	99.2	97.4	90.3	97.6	

TABLE 25

CRUDE PHENOL COMPONENT DATA

GC #	b.p. deg.C	b.p. deg.F	Component	Area% Over	Retention Time	Peak Area%	Elemental, atomic C	H	N	O	S
1	182	359	Phenol	47	75.85	47.08	6	6		1	
2	191	376	C1 Phenol	56	92.77	8.47	7	8		1	
3	202	396	C1 Phenol	79	98.20	23.53	7	8		1	
4			Methoxyphenol	81	102.14	1.88	7	8		2	
5			C2 Phenol	82	113.31	0.82	8	10		1	
6			C2 Phenol	84	116.32	1.96	8	10		1	
7			C2 Phenol	85	120.52	1.54	8	10		1	
8			C2 Phenol	89	121.13	3.51	8	10		1	
9			C2 Phenol	89	123.62	0.70	8	10		1	
10			C2 Phenol	91	127.76	1.04	8	10		1	

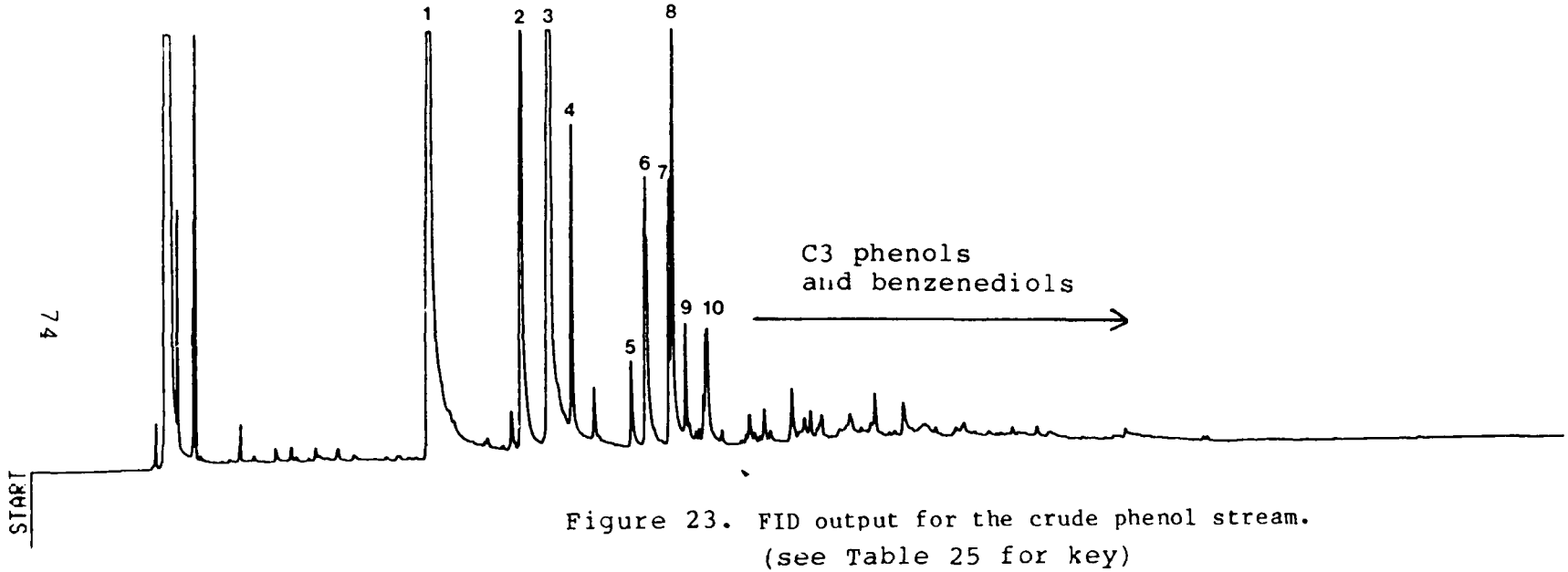


Figure 23. FID output for the crude phenol stream.
(see Table 25 for key)

True Boiling Point Distillation of Crude Phenols

In order to obtain a more complete picture of the GPGP crude phenol stream, a sample has been analyzed to obtain true boiling point distillation data. Nine fractions were collected during the distillation and these fractions have been analyzed to determine the compounds and compound types present in each fraction using GC/MS and proton NMR. The fractional distillation apparatus used to do the TBP distillation had a fractionating column that produced 12.5 theoretical plates (described in the Experimental Section).

The TBP distillation data is presented in Table 26 and Figure 24. The wt% in each collected fraction and the assigned fraction number are as indicated in the Table. The initial 4 wt% that distilled was mainly water. The second 3 wt% also contained water and was combined with the first 4 wt% as fraction 1. This separated into a water and oil phase. Only the oil phase of fraction 1 has been analyzed. Fractions 2 to 4 contained mainly phenol and also increasing amounts of o-cresol (from 9 to 20 wt%) in each fraction. Fraction 5 was over 90 wt% in phenol and cresols but also contained about 4 wt% of a methoxy compound. In fraction 6 the relative amounts of ortho-, meta-, and para-cresol were similar while fraction 7 contained smaller amounts of o-cresol. Fraction 8 contained dimethyl phenolics while fraction 9 (the bottom 33 wt%) contained mixed methylated dihydroxy aromatic compounds.

Proton NMR Data for the Various TBP Fractions

For complex mixtures containing many different compounds, proton NMR spectra of the mixture provide semi-quantitative data of functionalities present. However, in less complicated mixtures, one can often determine semi-quantitatively concentrations of individual compounds. Unique protons in phenol, the cresols, and methoxy-compounds exist which can be readily observed in unique positions in proton NMR spectra as previously described in the Experimental Section. Even the methyl protons in ortho-, meta-, and para-cresol are distinguishable as unique.

Fractions 2 to 8 contain primarily phenol and cresol proton NMR peaks as seen in Tables 27 and 28. The data on Table 27 enable a comparison of the NMR data for the total sample to the NMR data calculated from the wt% and peak area% values for the fractions on Table 28 (a proton mass balance) which appears to be good. As seen in this Table, the area% for alpha-methyl protons increases steadily from a low of 3.9% in fraction 2 to a high of 37.1% in fraction 8 indicating that increasing amounts of cresols are present. The amount of methoxyl functional groups present in each subsequent fraction also increases, since the methyl proton

TABLE 26

TRUE BOILING POINT DISTILLATION
OF GPGP CRUDE PHENOLS

Room Temp	22°C
Barometric Pressure	744.4 mm Hg
Specific gravity	1.070
Sample Weight	214.0 g

Distillation Curve

Distillate (ml)	Temp. (°C)	Time (min)	Rate (ml/min)	Fract. No.	Fract. wt%	Cum. Fract. wt% sum
0	54	0				
5	97	28.8	0.17			
10 (5%)	98	69.0	0.12		4.03	
15	98	123.0	0.09			
17 (8.5%)	178	145.3	0.09	1	3.11	7.14
25	178	151.3	1.33			
30	178.5	155.7	1.15			
35	179	159.9	1.19			
40 (20%)	179	164.8	1.01	2	10.96	18.10
45	179	168.9	1.22			
50	179.5	174.7	0.87			
55	180	180.2	0.91			
60 (30%)	180	186.7	0.77	3	9.75	27.85
65	180	192.8	0.81			
70	180	200.0	0.70			
75	180.5	206.3	0.79			
80 (40%)	181	212.8	0.77	4	9.26	37.11
85	182	221.0	0.61			
91	188	227.4	0.94			
94 (47%)	190	229.5	1.44	5	6.49	43.60
100						
102 (51%)	193			6	3.65	47.25
107	195	240.5	1.18			
111	195.5	244.5	1.00			
115	196	249.0	0.89			
120	196	255.5	0.77			
125	197	263.3	0.65			
130	197.5	269.0	0.87			
131 (65.5%)	198	270.5	0.67	7	13.08	60.33
135	198.5	274.5	1.00			
140	200	281.3	0.73			
142 (71%)	202	284.3	0.67	8	5.16	65.49
		Pot resid		9	32.99	98.48
		Recovery			98.48	

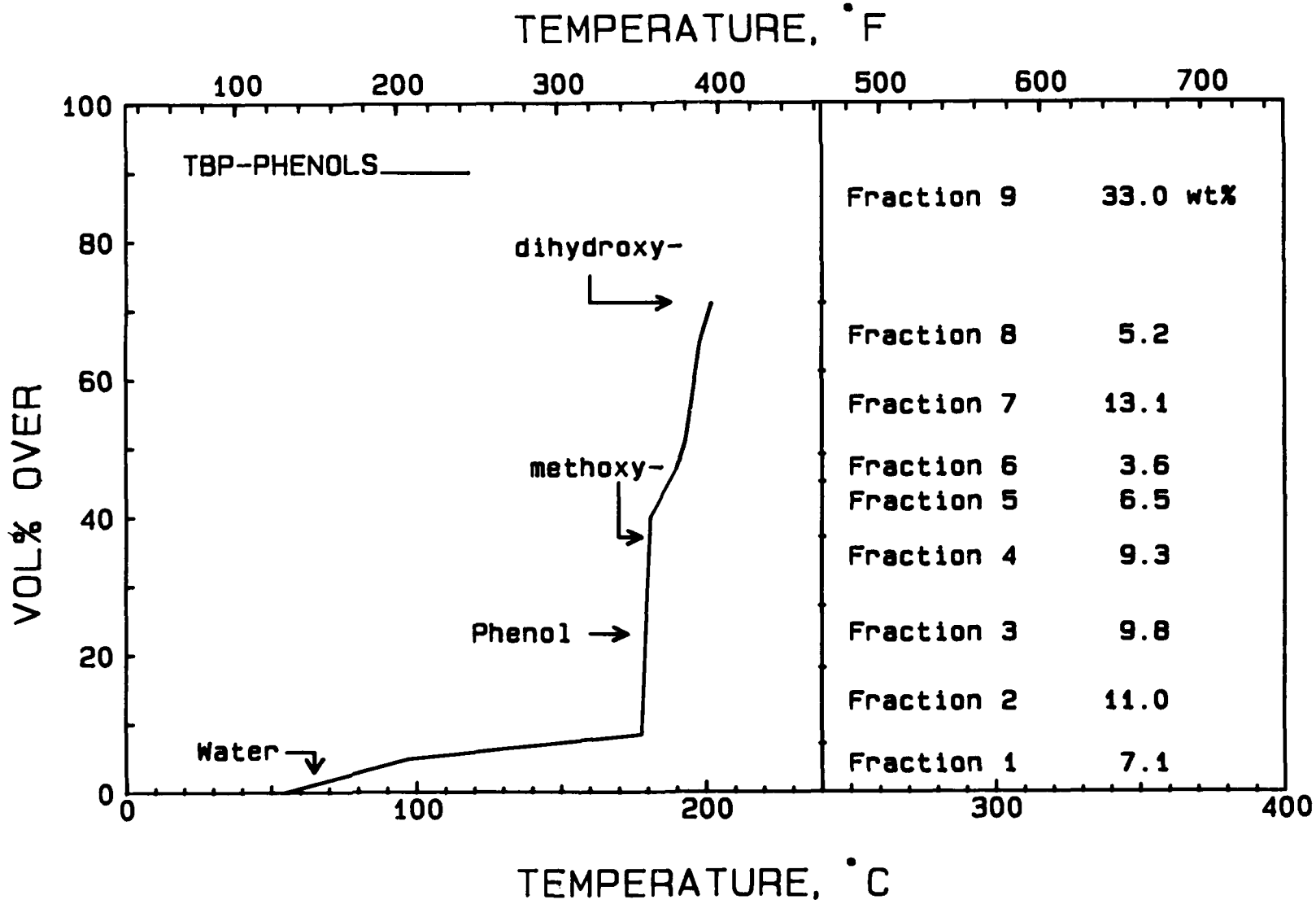


Figure 24. True boiling point distillation data summary for GPGP phenols.

TABLE 27

PROTON NMR DATA AND FUNCTIONAL GROUP ANALYSIS FOR DRIED GPGP PHENOLS

FUNCTIONAL GROUP	NMR REGION ppm	TOTAL PROTON Area %	SUM PROTON Area %
Aromatic	9.0-5.9	54.8	50.1
Phenolic	5.2-4.4	12.2	12.0
Methoxy	4.4-3.5	1.3	2.0
Alpha-Meth	3.3-1-9	23.6	24.2
Other		8.0	10.3
Total		99.9	98.6

TABLE 28

PROTON NMR ANALYSIS OF DRIED GPGP PHENOL TBP FRACTIONS

	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Fraction 6	Fraction 7	Fraction 8	Fraction 9
Temp., °C wt % of total	IBP-178 7.14	178-179 10.96	179-180 9.75	180-181 9.26	181-190 6.50	190-193 3.65	193-202 13.08	198-202 5.16	Pot Residue 33.00
NMR, area %									
Aromatic	30.1	77.3	75.1	72.7	62.8	52.6	47.1	44.0	33.2
Phenolic	4.0	15.4	15.2	15.3	13.5	11.0	10.9	10.5	11.8
Methoxyl	5.8	0.9	0.6	1.0	1.5	2.0	3.1	3.7	1.6
Alpha-Meth	21.7	3.9	6.4	8.2	19.0	31.0	35.1	37.1	36.2
Other	38.4	2.5	2.7	2.8	3.2	3.4	3.8	4.7	17.2
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

area percent increases, from 0.6% in fraction 2 to 3.7% in fraction 8. Actual changes in the spectra are depicted in Figures 25 to 29.

Fraction 1 (Figure 25) was a complex mixture due to the co-distillation of water which phase separated after cooling. The spectrum presented is for the dried oil phase which represents about half of fraction 1. A relatively large amount of methoxyl functional groups are present as are aliphatic functional groups especially when compared to the next fraction.

Fractions 2 to 4 were very similar showing increased amounts of o-cresol (9 wt%, 15 wt%, and 20 wt%, respectively) with the balance being phenol. Figure 26 depicts the spectrum of fraction 4 showing the pronounced alpha-methyl proton peak at 2.25 ppm which is characteristic of o-cresol.

The spectrum of fraction 5 (Figure 27) indicates the presence of meta- and para-cresol in addition to o-cresol (a total cresol content of about 49 wt% and phenol content of about 47 wt%). Trace amounts of dimethyl phenolics are indicated by the peaks at 2.14 and 2.17 ppm. About 4 wt% of a methoxyl-containing compound (possibly o-methylanisole) is indicated by the peak at 3.8 ppm. Fractions 6 and 7 are similar, but contain increasing amounts of cresols and methoxyl compounds.

The spectrum of fraction 8 (Figure 28) shows the disappearance of o-cresol and the definite appearance of dimethylphenolics. Fraction 9 is again more complex. The NMR spectrum (Figure 29) indicates the presence of aliphatics (peaks in the 0.3 to 1.4 ppm region) and more diverse alkylation (multiple peaks between 2 and 3 ppm). Also, the hydroxyl peak has shifted to higher values indicating the possible presence of dihydroxybenzenes.

Figure 30 depicts the spectrum of fraction 4 after adding 10.5 wt% of pure o-cresol. Calculations indicate that the cresol content calculated from NMR data has a range of plus or minus 10%.

GC/MS Component Analysis of TBP Fractions

The various true boiling point fractions were analyzed by GC and the component peaks were identified using MS and/or Retention Indices. Figure 31 is a composite of the GC profiles for fractions 1 to 9 for easy comparison. Table 29 presents the peak area% data for essentially all compounds eluting from aniline through naphthalene for fractions 2 to 8 and selected later eluting compounds in fraction 9.

Fraction 1 contains varied amounts of components due to the co-distillation of water. Numerous higher boiling compounds are

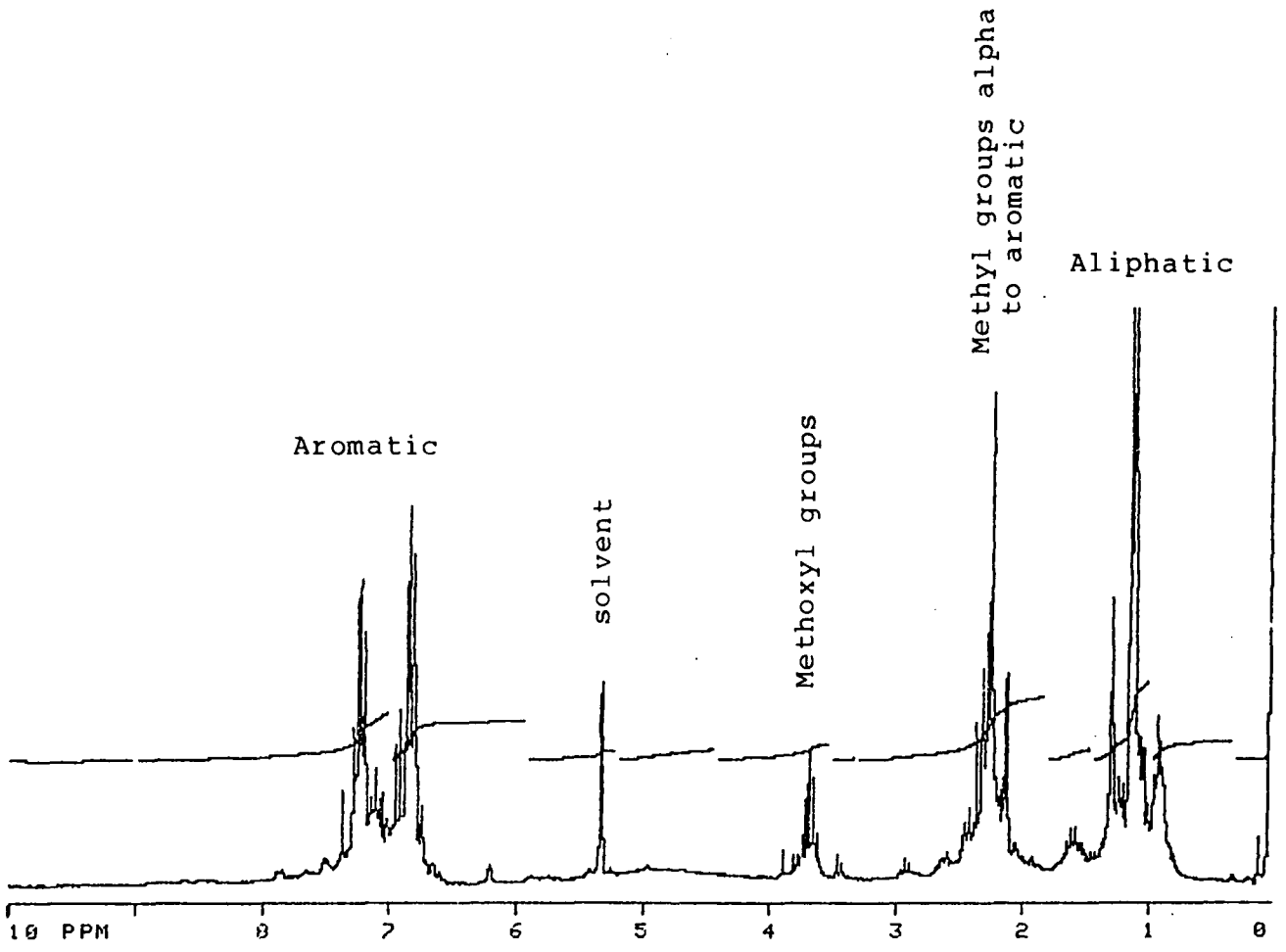


Figure 25. Proton NMR spectrum of TBP fraction 1 oil phase, IBP - 178°C (3.5 wt%).

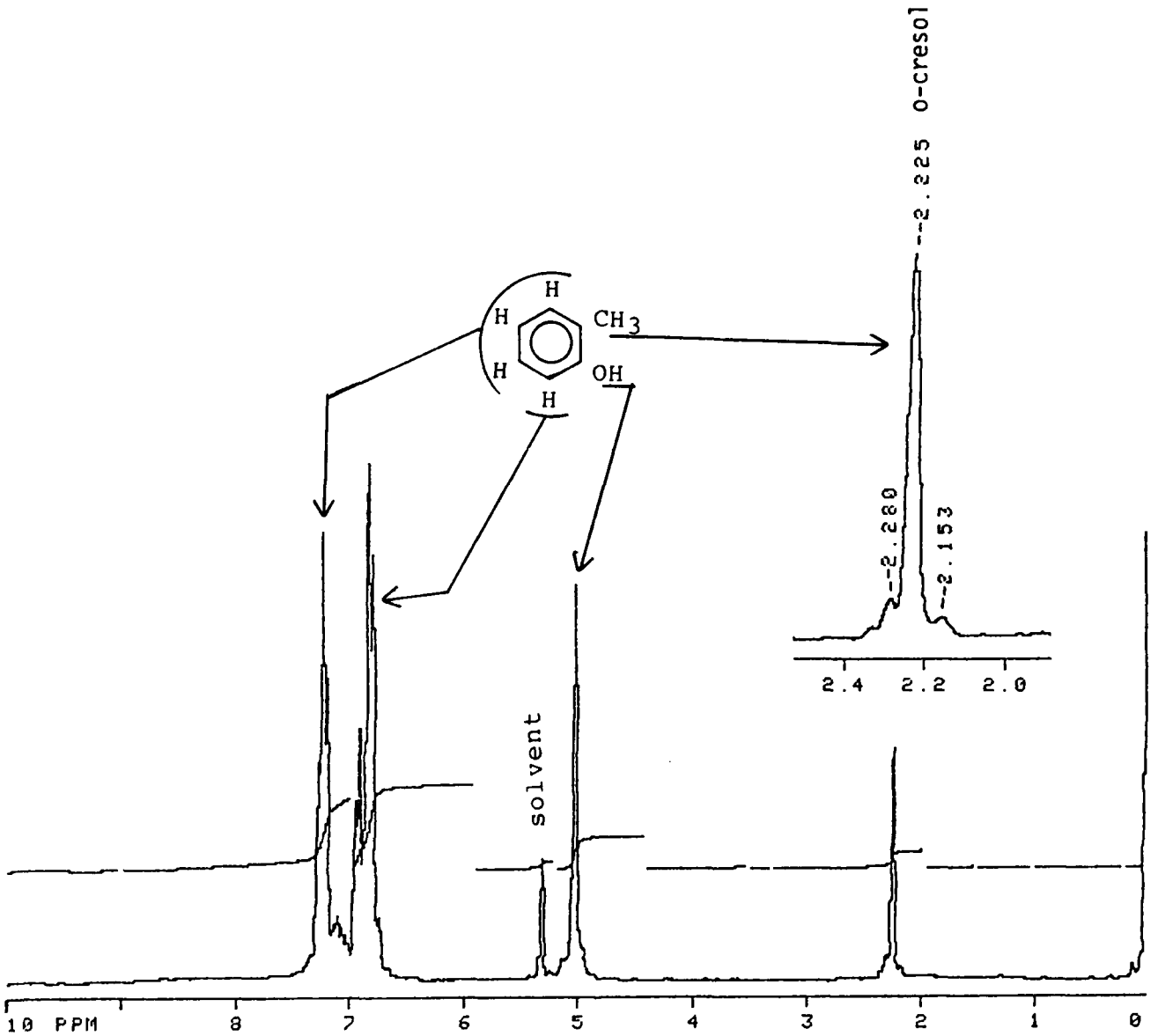


Figure 26. Proton NMR spectrum of TBP fraction 4, 180 - 181°C (9.3 wt%).

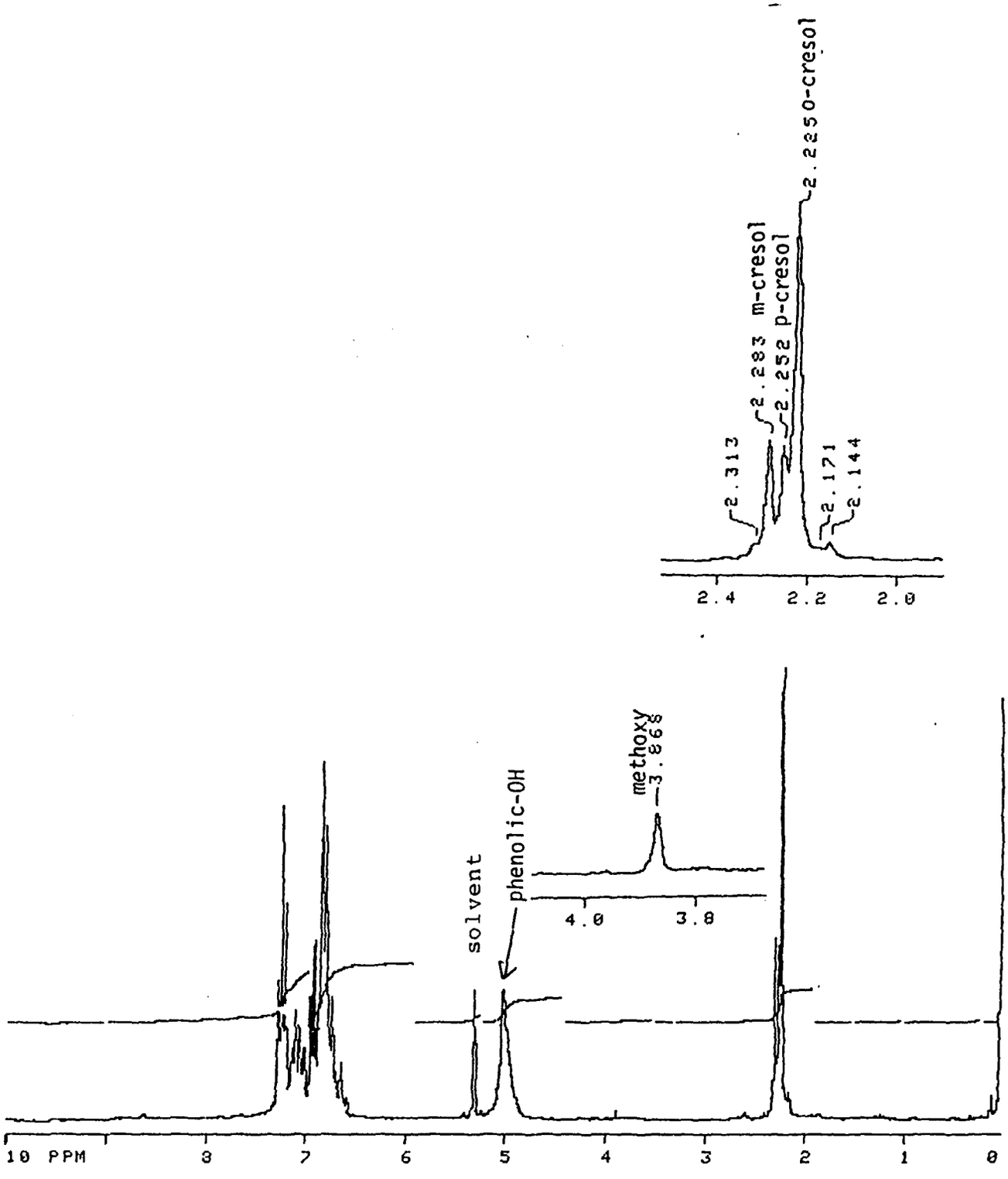


Figure 27. Proton NMR spectrum of TBP fraction 5, 181 - 190°C (6.5 wt%).

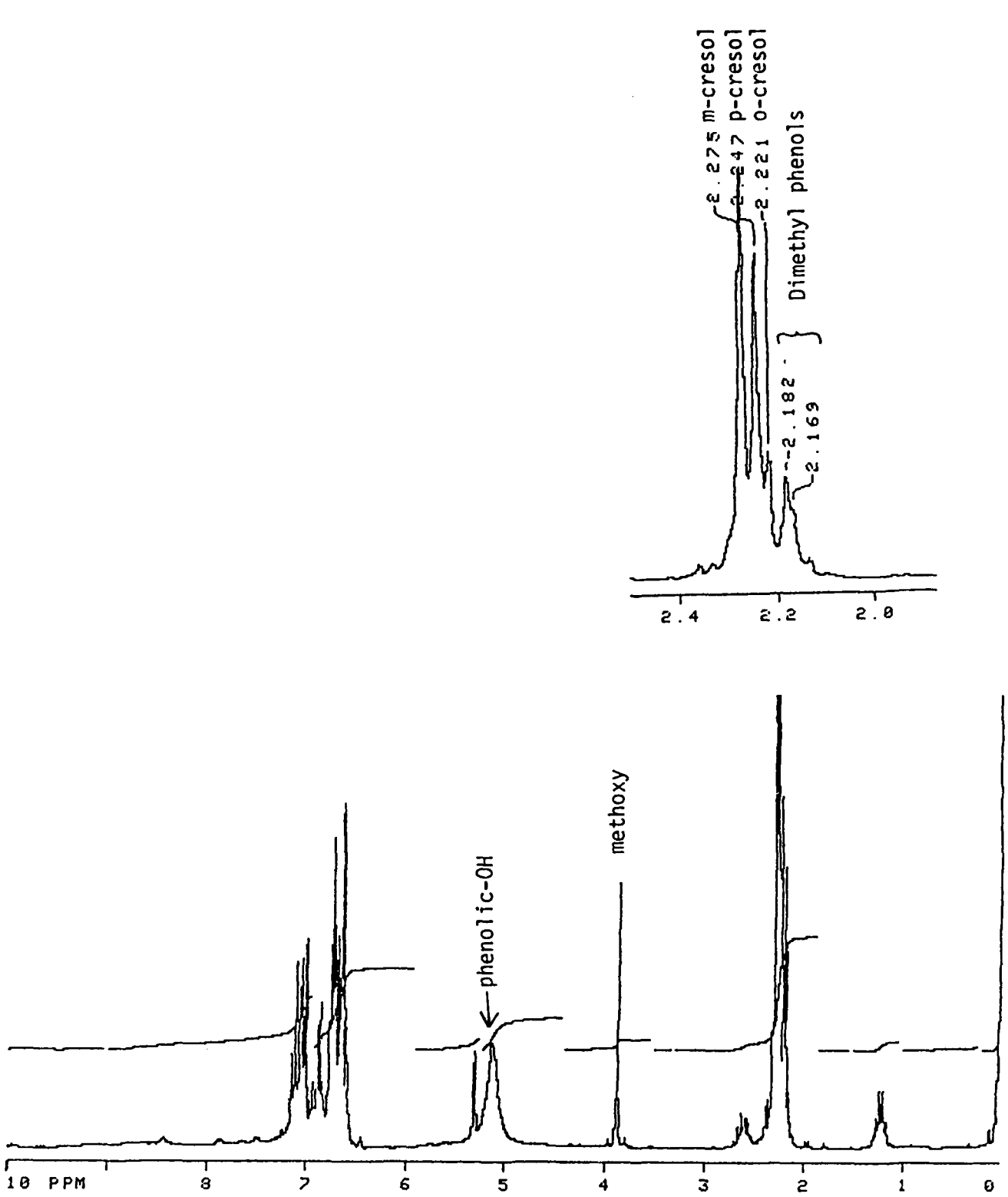


Figure 28. Proton NMR spectrum of TBP fraction 8, 198 - 202°C (5.2 wt%).

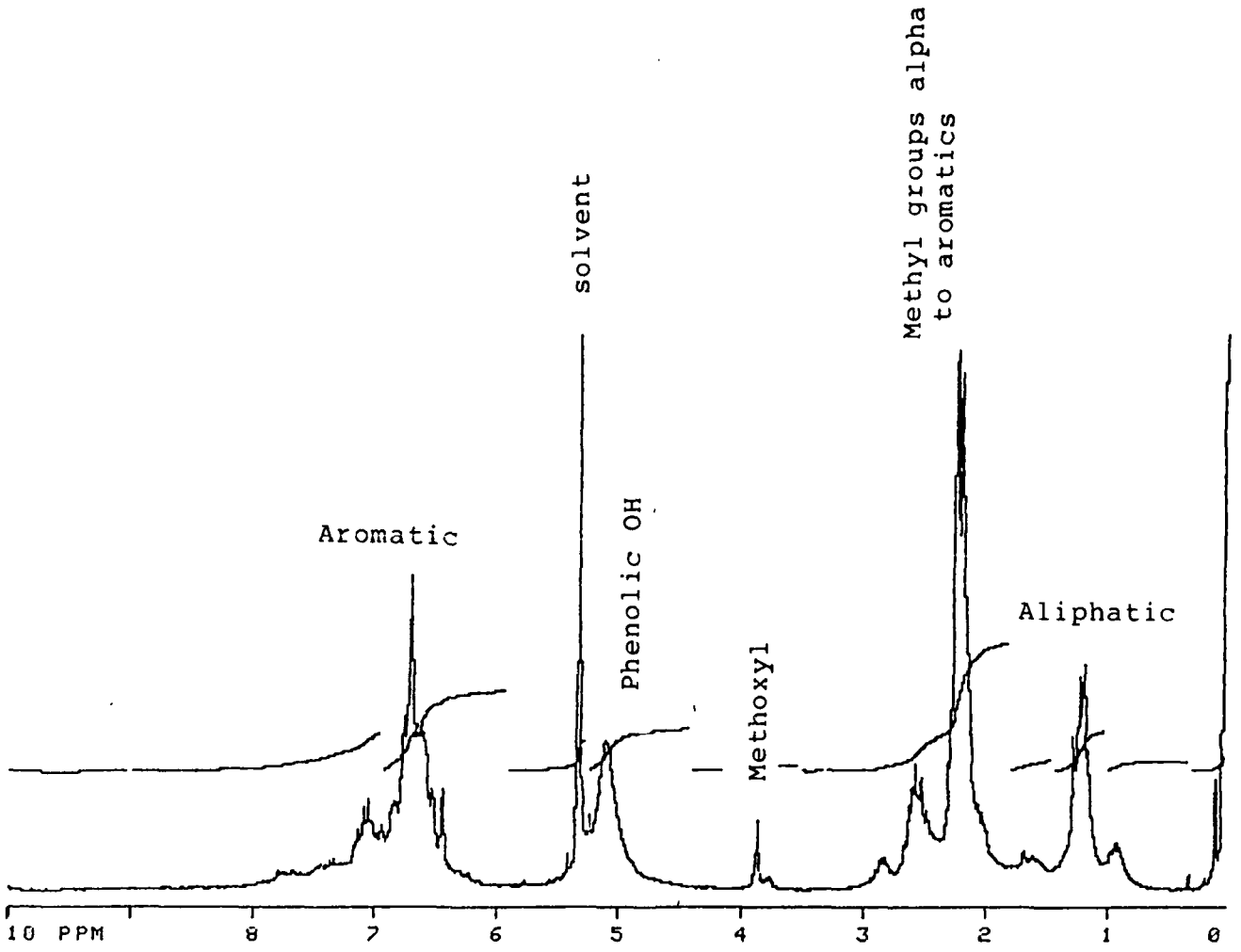


Figure 29. Proton NMR spectrum of TBP fraction 9, pot residue (33 wt%).

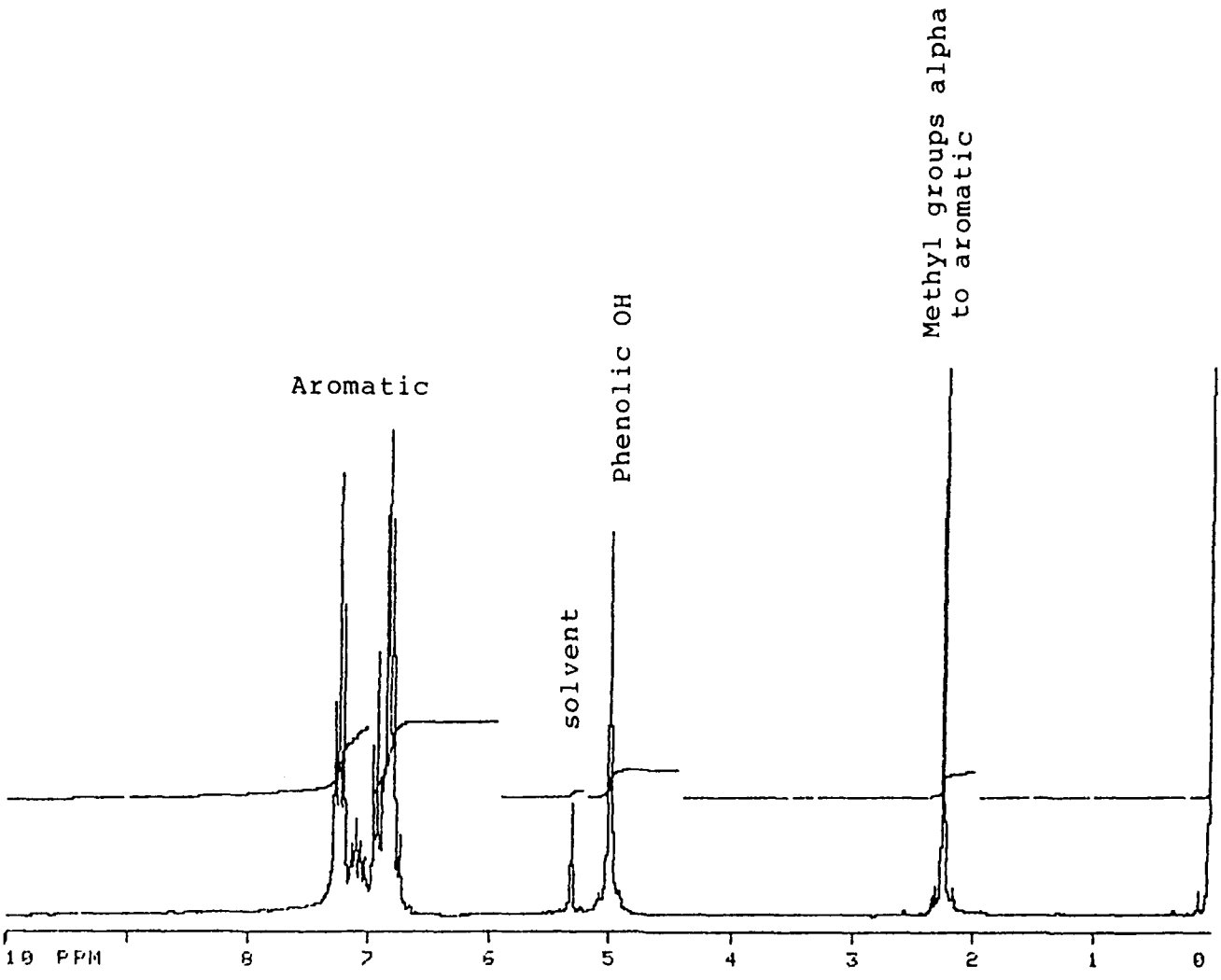


Figure 30. Proton NMR spectrum of TBP fraction 4 after addition of 10.5 wt% o-cresol.

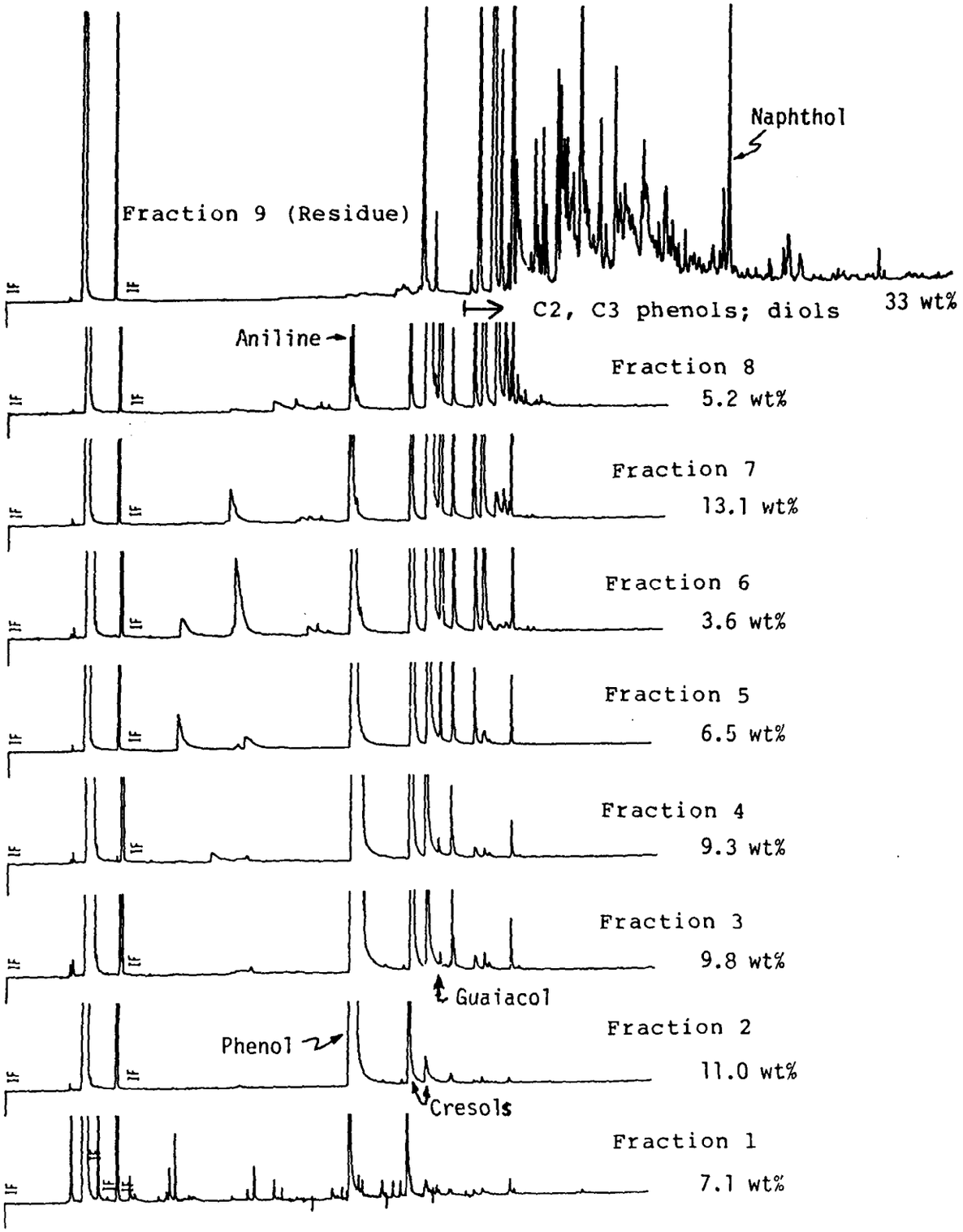


Figure 31. GC profiles of TBP distillation fractions of GPGP phenols. (see Table 24 for key)

TABLE 29

GC DATA FOR TBP FRACTIONS OF GPGP PHENOLS
Wt. % in Each Fraction

Compound Type	RT[a]	#[b] wt%[c]	1 7.1	2 11.0	3 9.8	4 9.3	5 6.5	6 3.6	7 13.1	8 5.2	9 33.0
Aniline	12.70							.49	.48		
Phenol	12.79		47.62	95.38	87.72	84.81	58.20	22.73	5.82	1.01	
C1 Phenol	14.97		12.96	4.10	10.58	13.00	24.30	20.08	9.04	1.22	.06
C1 Phenol	15.73		2.60	.381	1.26	1.62	14.53	49.08	71.38	65.44	3.54
Guaiacol	16.08		4.19		.02	.03	.43	2.04	4.17	6.13	.57
C2 Guaiacol	16.51		1.76	.086	.06	.13	.62	1.05	.89	.41	
C2 Phenol	17.31		.65	.025	.02	.01	.39	1.31	2.07	2.36	.22
C2 Phenol	17.61		.81		.03	.03	.16	.56	2.15	9.21	2.48
C2 Phenol	17.64							7.48	2.09	5.06	2.12
C2 Phenol	18.12								.13	2.46	6.60
C2 Phenol	18.19								.31	2.71	12.26
C2 Phenol	18.43							.02	.16	1.16	1.76
C3 Phenol	18.64								.06	.19	.06
Naphthalene	18.70		1.34	.03	.08	.07	.24	.51	.60	.62	.38
C2Phenol	18.23										4.39
	18.87		.37							.22	2.04
Resorcinol	18.99									.07	2.32
C3 Phenol	19.14									.10	
C3 Phenol	19.59									.04	2.13
C3 Phenol	19.75									.08	1.80
C1-diol	21.38										6.84
C1-diol	22.64										1.79
C2-diol	22.83										1.31
C2-diol	23.67										2.09
	23.78										2.48
Naphthol	26.85										3.26

[a] Retention time.
[b] Fraction number.
[c] The wt% of total sample.

present (even guaiacols) in larger amounts than in later distillation fractions. Fractions 2 to 8 show increasing amounts of higher boiling compounds as expected in a distillation where water was not present. Phenol was a maximum (95.4 area%) in fraction 2 and only 5.8 area% in fraction 8. Small amounts of aniline (about 0.5 area%) were observed in fractions 7 and 8. A small shoulder on the phenol GC peak (see Figure 31) indicates a trace amount of aniline was present in fraction 6.

Guaiacol was present in all fractions ranging from 0.02 area% in fraction 2 to 6.13 area% in fraction 8. A C2-guaiacol was also possibly present (0.09 to 1.8 area%) in these fractions. Cresol content maximizes in fractions 6 and 7 (69.2 and 80.4 area%, respectively). A small amount of naphthalene (0.32 to 1.3 area%) was present in all fractions. Fraction 8 contained measurable amounts of a dihydroxy aromatic, resorcinol, while fraction 9 contained numerous dihydroxybenzenes. Fraction 9 (the distillation bottoms) also contains various amounts of dimethyl- and trimethylhydroxybenzenes and higher hydroxy aromatics such as naphthols.

The following conclusions are suggested from the GC/MS data of the TBP distillation fractions:

1. The initial distillate (7.1 wt% including about 3.5 wt% of water) is a broad mixture of compounds due to the codistillation of water.

2. The next 30.1 wt% of distillate contains very little guaiacol (under 0.03 area%) but about 0.1 area% of a methylguaiacol and over 97 area% of phenol and cresol (over 85% phenol).

3. The final 16 wt% of distillate is also mainly phenol and cresol (over 66 area% cresol), but also contains sizable amounts of guaiacol (up to 6 area%) and up to 25 area% of mixed methyl- and dimethylcresols.

4. The bottom 33 wt% contains a wide mixture of hydroxy- and dihydroxyaromatics with various degrees of alkylation.

5. The higher concentrations of the guaiacols and naphthalene in the initial distillate indicates that these contaminants may be removed by additional steam distillation prior to the recovery of phenol and cresol.

Aliphatic, Aromatic, and Polar Fractions

Separation of complex mixtures into compound type fractions followed by analyses of the fractions enables better comparisons. The crude phenol stream has been separated into aliphatics, aromatics, and polars by solvent elution from a silica gel column. Table 30 presents yield and elemental data for the samples and fractions. The phenols contain only 0.5 wt% aliphatics and 1.8 wt% aromatics (light boiling materials were probably lost during rotovaping to remove the eluting solvent) with most of the oxygen in the polars.

Figure 32 depicts the NMR data for the sample and fractions. Note that aliphatic fraction is essentially void of aromatics indicating that good separations were obtained. The crude phenol contains few aliphatics (0.1 to 1.5 ppm region) and contains mainly aliphatic protons on carbon alpha to an aromatic ring (1.9-3.3 ppm region) as in cresols. The polar fraction contains aromatic protons (5.9 to 9 ppm region) and most are associated with phenolics.

TABLE 30

ELEMENTAL ANALYSES OF TOTAL AND COLUMN FRACTIONS

Crude Phenols	Fraction wt%	Elemental Composition, wt% C	H	N	S	O+S	KF-water[a]
Total	100.0	72.18	7.40	0.28	0.04	20.05	4.48
Aliphatics[b]	0.5	.	.	.	.	.	.
Aromatics	1.8	81.41	7.50	0.29	NA[c]	10.80	NA
Polars	92.5	73.62	7.32	0.32	NA	18.74	NA
Recovery	99.3[d]						

[a]Karl-Fisher Analysis in wt% of total sample.
[b]Sample too small for elemental and KF-water analysis.
[c]NA indicates not analyzed.
[d]Water is not recovered from the column but is included in the total recovery.

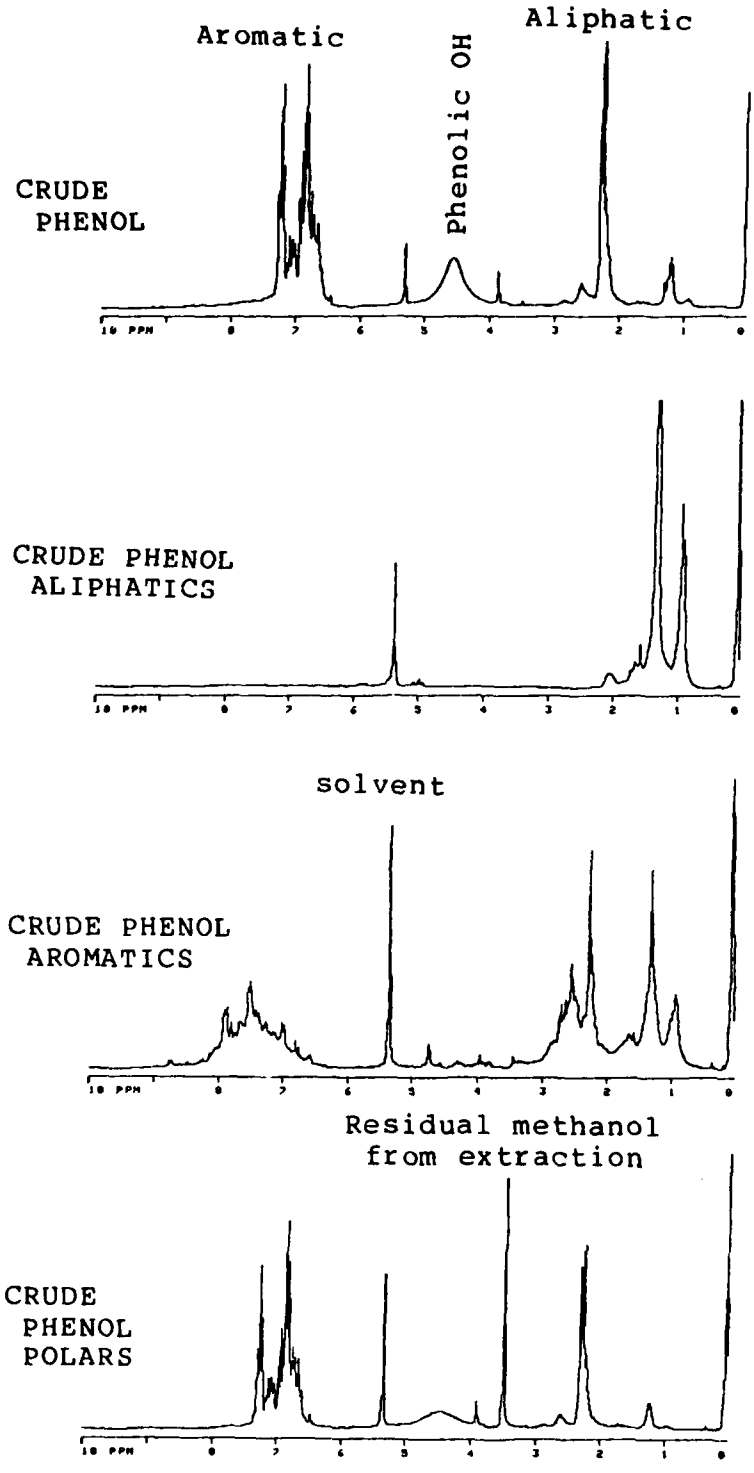


Figure 32. NMR spectra of the crude phenol stream and its three short column fractions.

RECTISOL NAPHTHA STREAM

The rectisol naphtha stream is too light for use as a jet fuel. Single-ring aromatics such as benzene, toluene, and xylene (BTX) together may account for up to 50 vol% of the stream, and have considerable value. In its raw form, the stream possesses an extremely powerful odor which is relatively easy to remove.

Characterization of the Rectisol Naphtha Stream

The rectisol naphtha stream was analyzed using a variety of techniques including distillation, gas chromatography (GC), gas chromatography coupled with mass spectrometry (GC/MS), and carbon-13 and proton nuclear magnetic resonance spectroscopy (C13- and H-NMR, respectively).

Deodorization of the Rectisol Naphtha Stream

The stream was analyzed with GC/MS and found to contain many sulfur compounds including thiols, thiobismethane, and thiophenes, all of which can cause very unpleasant odors at very small concentrations. The two methods studied for the removal of these sulfur compounds were a sulfuric acid wash and a sodium hydroxide extraction. Figure 33 shows the total ion chromatogram (obtained with a Hewlett-Packard 5985B GC/MS) of the stream before and after the acid wash, and demonstrates that most of the thiophenes have been removed.

The pH of the as-received naphtha was low (between 2-5 as measured with pH paper). Simply exposing a sample to air and allowing volatile material to escape reduced the odor. A caustic wash also reduced the odor of the naphtha. However, a caustic wash containing a small amount of copper sulfate eliminated the unacceptable odor. To 100 mL rectisol-naphtha, 50 mL 0.1 M NaOH and 2 mL 0.00025 M CuSO4 were added and stirred vigorously for up to 4 hours. The reaction was greatly facilitated by the addition of about 2 mL of 0.0015 M quinoline solution to the CuSO4 before addition to the rectisol-naphtha. This provided a deodorized sample.

In order to determine which components had been removed by the caustic-copper wash, as-received and deodorized rectisol naphtha samples were analyzed by GC and GC/MS. The samples were not diluted before injection because a large solvent peak would probably mask one or several of the many volatile sample component peaks. Therefore, a very small sample injection was required to prevent exceeding the sample capacity of the column. A microsyringe capable of injecting 0.02ul was used in this analysis. Samples were introduced into the GC and GC/MS via the split/splitless injection port (operating in the split mode). The split ratio was approximately 1:100 with H_2 carrier. The column oven temperature was initially held at -20^{o}C for 2 minutes

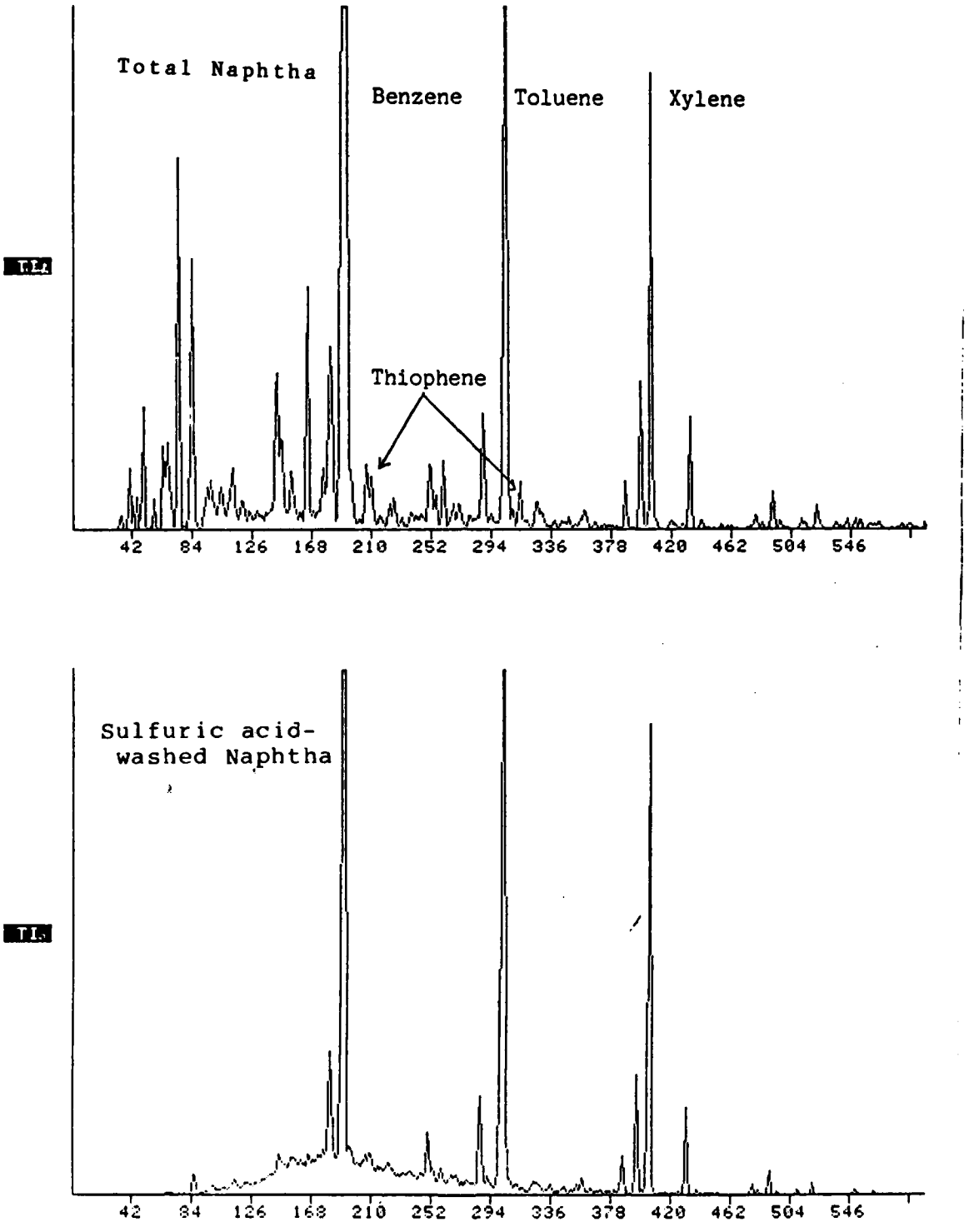


Figure 33. Components in rectisol naphtha before (top) and after (bottom) sulfuric acid wash.

and then ramped to 320°C at 6°C/min. Table 31 lists the compounds that have been identified and their GC numbers which corresponds to the numbered peaks in Figures 34-36. Figures 34 and 35 show the total ion chromatograms (TICs) obtained from the analysis of the two samples. Figure 34 is the TIC of the rectisol naphtha before treatment for odor removal and Figure 35 is the TIC of the deodorized rectisol naphtha. Figure 36 is the flame ionization detector (FID) chromatogram from which area% data were obtained. It is apparent in comparing these figures that a portion of the material in the untreated rectisol naphtha is removed. The deodorized sample has fewer "light" components and no low molecular weight sulfur species. These sulfur compounds along with the thiophenes probably account for the odor of the rectisol naphtha. Ethanethiol has a minimum detectable odor concentration of 1 part in 50 billion parts of air (Merck Index, page 490). It also appears that this deodorization process removes some of the C2 and C3 benzenes.

TABLE 31

RECTISOL NAPHTHA COMPONENT DATA

GC #	b.p. deg.C	------ deg.F	Component	Area% Over	Retention Time	Peak Area%	Elemental, atomic C	H	N	O	S
1				0	25.79	0.26	4	8			
2				0	26.45	0.22	4	8			
3				1	28.08	0.15	4	8			
4	6.0	43	Methanethiol	1	29.04	0.21	1	4			1
5				1	30.10	0.15	4	8			
6				1	35.46	0.00	5	10			
7	36.0	97	n-Pentane	1	38.65	0.24	5	12			
8				2	43.45	0.31	5	10			
9	52.6	127	Acetone	4	46.39	2.28	3	6		1	
10				4	48.27	0.25	5	8			
11				5	49.13	0.44	5	10			
12				5	51.02	0.25	5	10			
13	37.3	99	Thiobismethane	5	52.17	0.16	2	6			1
14				6	52.71	0.86	5	10			
15	37.0	99	Ethanethiol	6	54.93	0.21	2	6			1
16				6	58.26	0.24	5	6			
17				6	59.13	0.15	5	8			
18				7	63.36	0.55	5	8			
19				7	64.61	0.13	6	12			
20				7	66.27	0.42	5	10			
21				8	68.52	0.47	6	12			
22				8	70.51	0.11	6	14			
23				8	73.59	0.18	6	14			
24				9	77.65	0.91	6	12			
25	68.0	154	n-Hexane	10	80.79	1.24	6	14			
26	79.6	175	2-Butanone	12	82.37	1.45	4	8		1	
27				12	83.22	0.33	6	12			
28				13	84.00	0.33	6	10			
29				13	84.82	0.61	6	12			
30				13	86.00	0.11	6	12			
31				14	90.49	0.81	6	12			
32				14	93.42	0.00	6	12			
33				14	96.44	0.21	6	8			
34				14	98.45	0.17	6	8			
35				16	100.69	1.30	6	10			
36				16	103.07	0.60	6	12			
37	80.1	176	Benzene	63	105.60	46.60	6	6			
38	84.2	184	Thiophene	63	107.13	0.57	4	4			1
39				64	108.27	0.18	6	8			
40	83.0	181	Cyclohexene	64	110.85	0.66	6	10			
41				65	112.31	0.20	7	14			
42				65	113.38	0.13	7	14			

TABLE 31 (Cont.)

RECTISOL NAPHTHA COMPONENT DATA

GC #	b.p. deg.C	deg.F	Component	Area% Over	Retention Time	Peak Area%	Elemental, atomic C	H	N	O	S
43				65	114.47	0.15	7	14			
44				66	116.70	1.05	7	14			
45				67	119.97	1.51	7	12			
46				68	122.95	0.24	7	14			
47				68	124.13	0.30	7	12			
48				68	125.75	0.21	7	14			
49				69	126.82	0.98	7	14			
50	98.4	209	n-Heptane	69	131.44	0.27	7	14			
51				70	133.58	0.44	7	12			
52				70	139.89	0.47	7	12			
53				70	140.62	0.21	7	12			
54				71	141.05	0.13	8	16			
55	110.6	231	Toluene	88	145.17	17.57	7	8			
56				88							
57				88							
58				88							
59			#56 - 63 total	90		1.61					
60				90							
61				90							
62				90							
63				90							
64	126.0	259	C8H18	91	156.81	0.83	8	18			
65				91							
66				91							
67				91							
68				91							
69			#65 - 73 total	91		0.79					
70				91							
71				91							
72				91							
73				91							
74			C2 Benzene	92	177.95	0.94	8	10			
75				92		0.01					
76			C2 Benzene	95	180.85	2.50	8	10			
77			#77 - 78 total	95		0.18					
78				95							
79			Benzene-C2	96	188.57	0.62	8	10			
80	150.8	303	C9H20	96	190.83	0.27	9	20			
81				96							

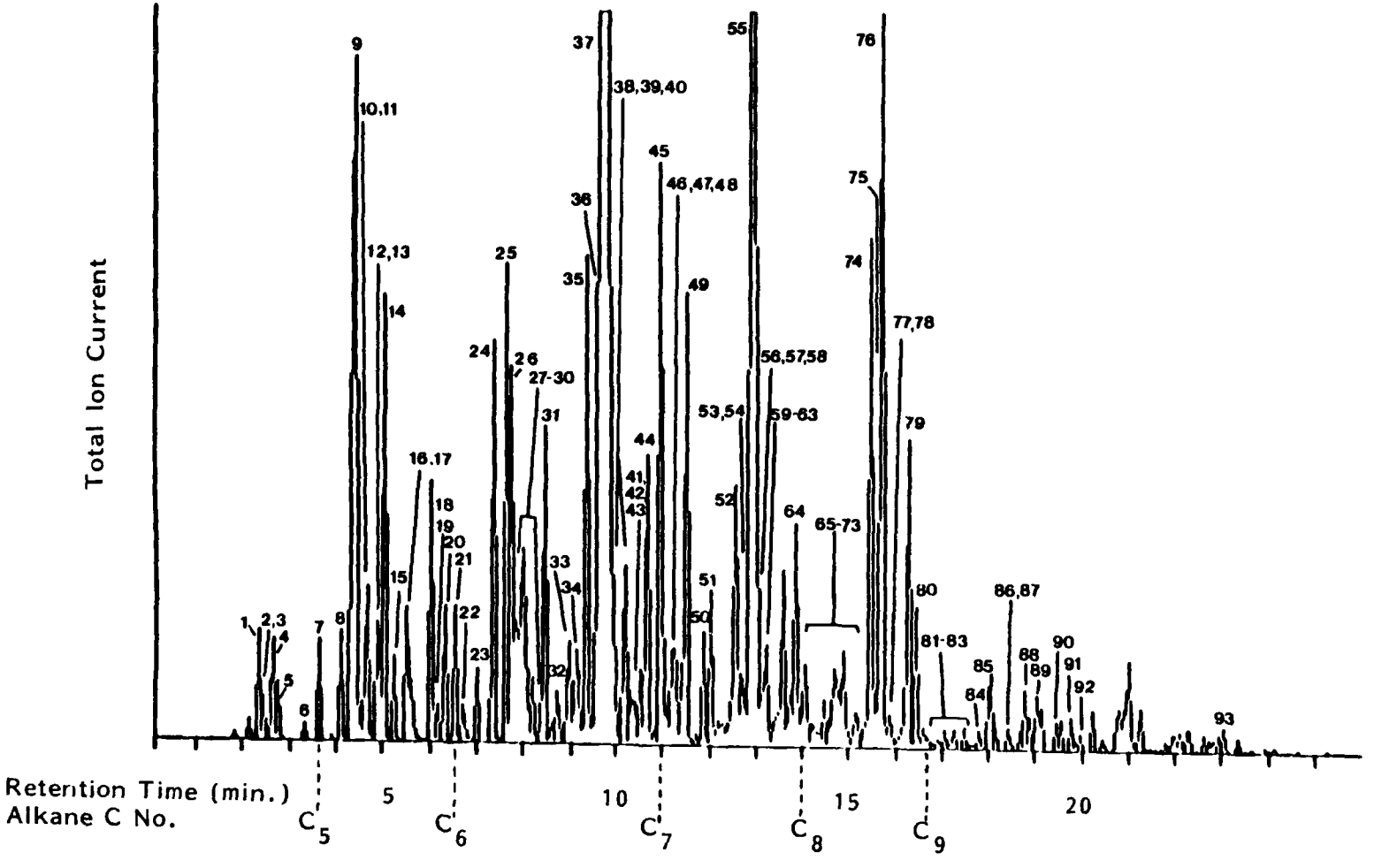


Figure 34. GC/MS analysis of rectisol naphtha.
(see Table 31 for key)

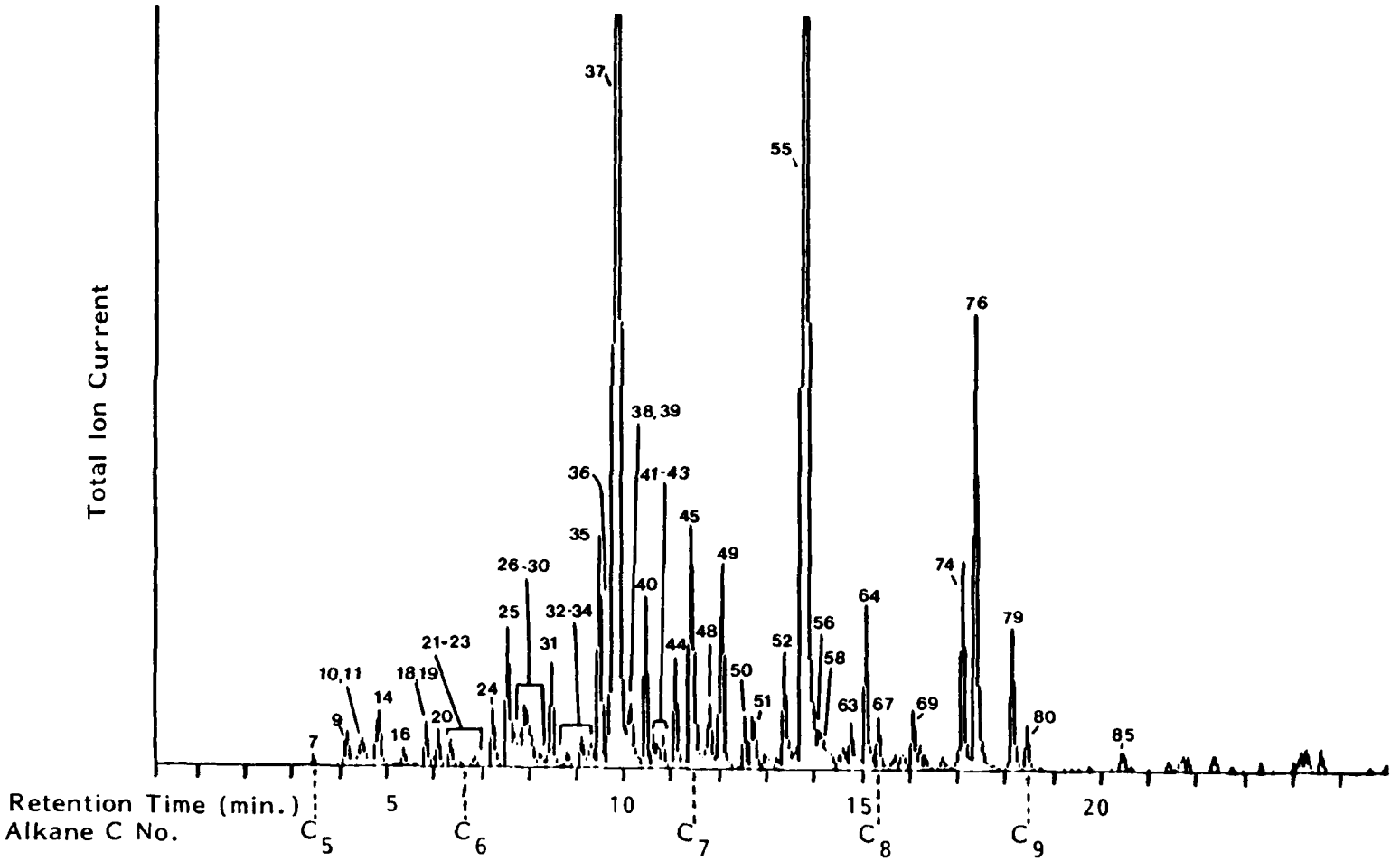


Figure 35. GC/MS analysis of deodorized rectisol naphtha.
(see Table 31 for key)

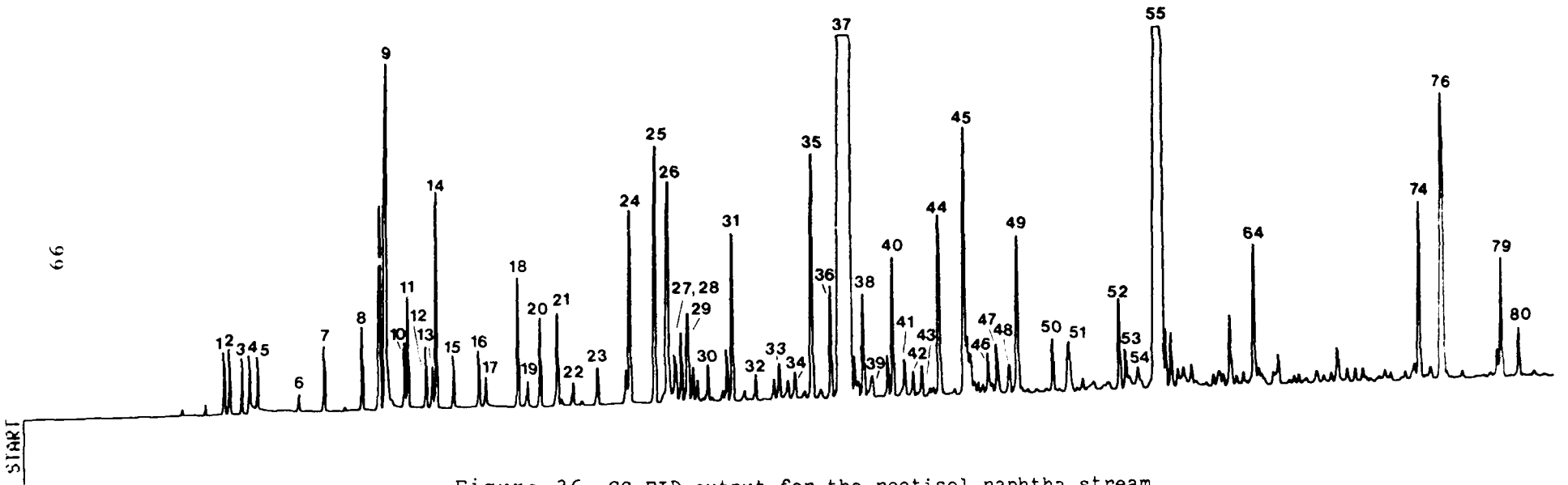


Figure 36. GC-FID output for the rectisol naphtha stream.
(see Table 31 for key)

Elemental Analysis of Rectisol Naphtha

Table 32 compares elemental data for rectisol naphtha with elemental data for the two other GPGP by-product streams and AV Jet A (commercial jet fuel). The naphtha is the closest to jet fuel in hydrogen content of the three by-product streams. However, as will be seen, it is much more volatile. Table 33 displays elemental data for three rectisol naphtha replicate samples for comparison.

TABLE 32

ELEMENTAL COMPOSITION BY WT% OF GPGP BY-PRODUCTS AND AV JET A

Element	Tar oil	Crude Phenol	Rectisol Naphtha	AV Jet A
Carbon	83.76	72.18	87.65	87.68
Hydrogen	8.83	7.49	10.12	14.30
Nitrogen	0.52	0.28	NA	0.06
Sulfur	0.39	0.04	NA	0.17
Oxygen[a]	6.50	20.01	2.23	-2.21
Atomic H/C	1.27	1.25	1.39	1.96

[a]Oxygen was determined by difference. NA means not analyzed.

Volatility of the Rectisol Naphtha Stream

As illustrated in Table 34, approximately 50 vol% of the stream is volatilized at 87°C and approximately 95 vol% is volatilized at 132°C. The Table compares D86 distillation data for the UNDEMRC rectisol naphtha sample obtained for this contract with different rectisol naphtha samples analyzed by ANG. Figure 37 presents D86 distillation profiles comparing data from all three GPGP by-product streams and AV Jet A.

The rectisol naphtha stream contains many highly volatile components including significant quantities of acetone, hexane, and 2-butanone, all of which are lost or greatly reduced in concentration as a result of deodorization (see Figures 34 and 35, and Table 31). In reviewing this data, it should be noted that there is often a large difference between area% and wt%, especially concerning oxygen-containing compounds. The difference derives from the way the flame ionization detector (FID) in the GC responds to different compounds.

TABLE 33

RECTISOL NAPHTHA ELEMENTAL ANALYSIS[a,b]

NO. SAMPLE	1 ERC		2 ANG		3 ANG	
	AR	mf	AR[e]	mf	AR	mf[e]
wt% C	87.65		86.56	87.00	86.00	86.43
H	10.12		9.01	9.00	9.00	8.99
N	0.00		0.30	0.30	0.20	0.20
S	NA		1.49	1.50	1.50	1.51
O[f]	2.23		2.64	2.20	3.30	2.87
total	100.0		100.0	100.0	100.0	100.0
water			0.50		0.50	

[a]Data obtained from various references as listed below.
[b]AR is as received and mf moisture free.
[e]Calculated values, NA means not available.
[f]Oxygen by difference.

No. 1: ERC 2nd qtrly Table 2.1
No. 2-3: ANG Memorandums 1/26/87 and 9/16/86 respectively.

TABLE 34

RECTISOL NAPHTHA D86 DISTILLATION DATA[a]

NO. SAMPLE	1 ERC		2 ANG		3 ANG	
Sp Gr	0.821		0.825		NA[b]	
ASTM D86	°C	°F	°C	°F	°C	°F
IBP	43	109	38	100	64	147
5	63	145			77	170
10	69	156	49	120	79	174
20	76	169	60	140		
30	79	174	71	160	86	186
40	83	181				
50	86	187	82	180	92	197
60	89	192				
70	94	201	91	195	101	214
80	102	216	102	215		
90	119	246	110	230	126	258
95	132	270			148	298
Max Vol	96	96	98	98	98	98
Max Temp	132	270	132	270	166	331

[a] Data obtained from the various references as listed below
No. 1: ERC 2nd qtrly Table 2.1
No. 2: ANG Memorandum, 9/16/86
No. 3: ANG letter, 10/9/8555

[b] NA means not available

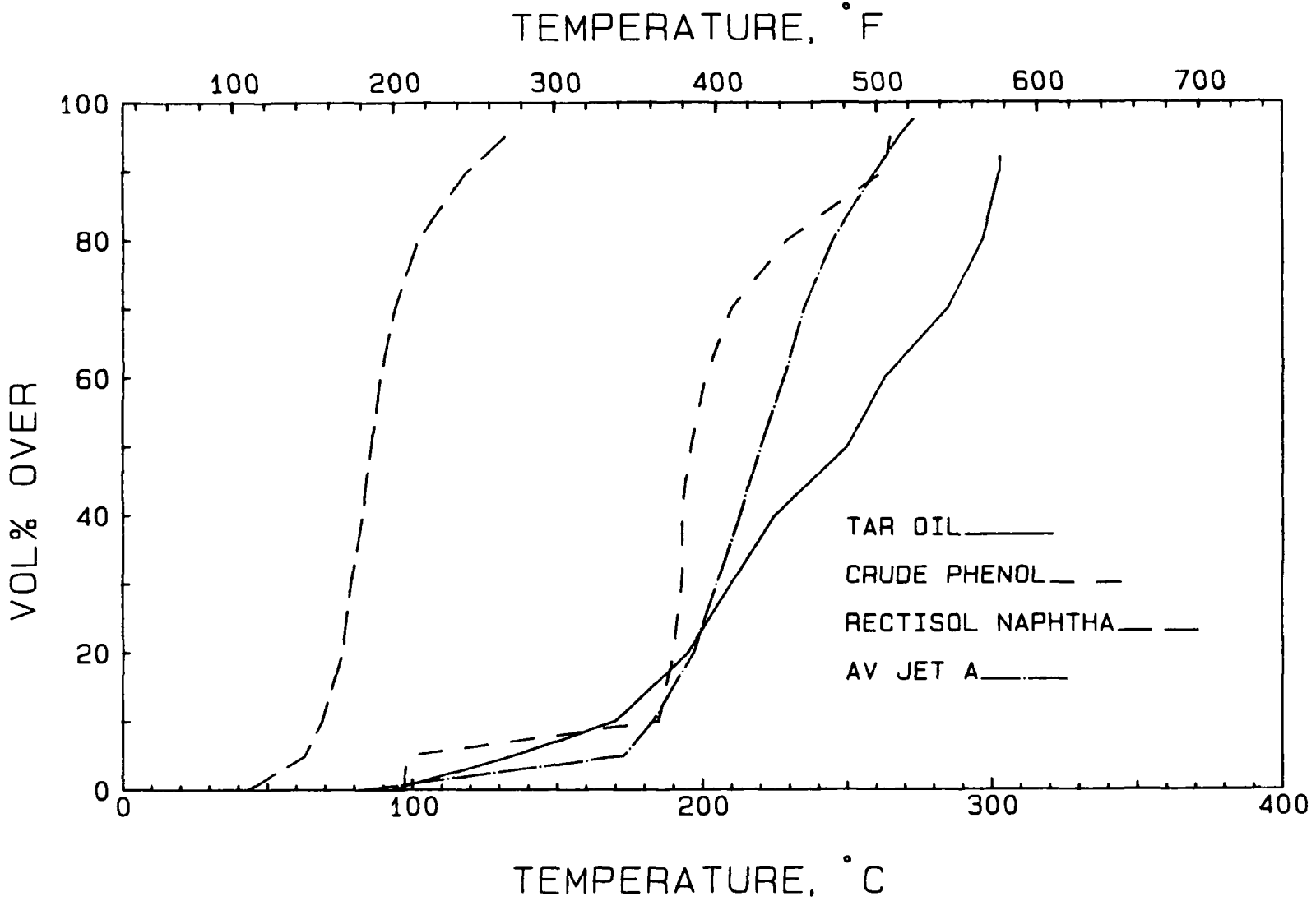


Figure 37. ASTM D86 distillation profiles of tar oil, crude phenol, rectisol naphtha, and AV Jet A.

GC/FID Analysis of Rectisol Naphtha

As an example of how an FID responds to different compounds, suppose that a two-component solution containing equal weights of acetone and toluene was injected into a GC equipped with an FID detector. Since an FID is essentially a carbon-hydrogen unit counter and doesn't respond in the same manner to carbon-oxygen units, the GC report would not record the presence of 50 area% for each compound, but rather, approximately 69 area% toluene and 31 area% acetone. In the case of the above example, the response factors for acetone and toluene are 0.49 and 1.07, respectively. The wt% acetone in the example solution can be calculated from the GC report by the following formula:

$$(31/0.49) / (69/1.07 + 31/0.49) = 50 \text{ wt\%}.$$

Referring to the data in Table 31, while the wt% acetone is approximately twice as great as its area%, the wt% benzene, toluene, and xylene may be up to 8 % less than their respective area%'s.

Analysis of Rectisol Naphtha for BTX Content

Three samples obtained earlier than the one previously discussed of rectisol naphtha from the GPGP were analyzed for benzene, toluene, and xylene content using GC and calibrated standards. While GC analysis using response factors can provide reasonable approximations of individual component concentrations, the use of calibrated standards enables more precise, more reliable quantitation. The analysis was performed using a 60 meter DB-1701 narrow bore capillary column. The GC temperature was held at 40°C for 3 minutes, then ramped at 6°/minute to 200°C. A split injection of 0.1 uL was used with a split ratio of approximately 1:100. Five standards ranging in concentration from 1:100 dilution to 1:1 dilution with methylene chloride were used to obtain a calibration curve for benzene, toluene, and the three xylenes. Two of the three xylenes (meta- and para-) did not resolve under these conditions and are reported as a combined value. Samples of approximately 70 mg were diluted to 10 mL with methylene chloride and 50 uL of an octane internal standard solution. Each sample was analyzed in duplicate. The results are shown in Table 35.

TABLE 35

QUANTITATION OF BTX CONTENT IN RECTISOL NAPHTHA

Sample	wt% Benzene	wt% Toluene	wt% m-, p-Xylene	wt% o-Xylene
Rectisol 1	32.5	13.4	2.7	0.8
Rectisol 2	29.2	12.0	2.3	0.7
Rectisol 3	21.4	9.3	1.9	0.6

NMR Analysis of the Rectisol Naphtha Stream

Figure 38 and Table 36 present NMR data. The proton NMR spectra in Figure 38 compare the three GPGP by-product streams and show that while the naphtha and phenol streams contain simple substituted benzene rings, the tar oil is rich in multiple aromatic ring systems (6.5-8 ppm region).

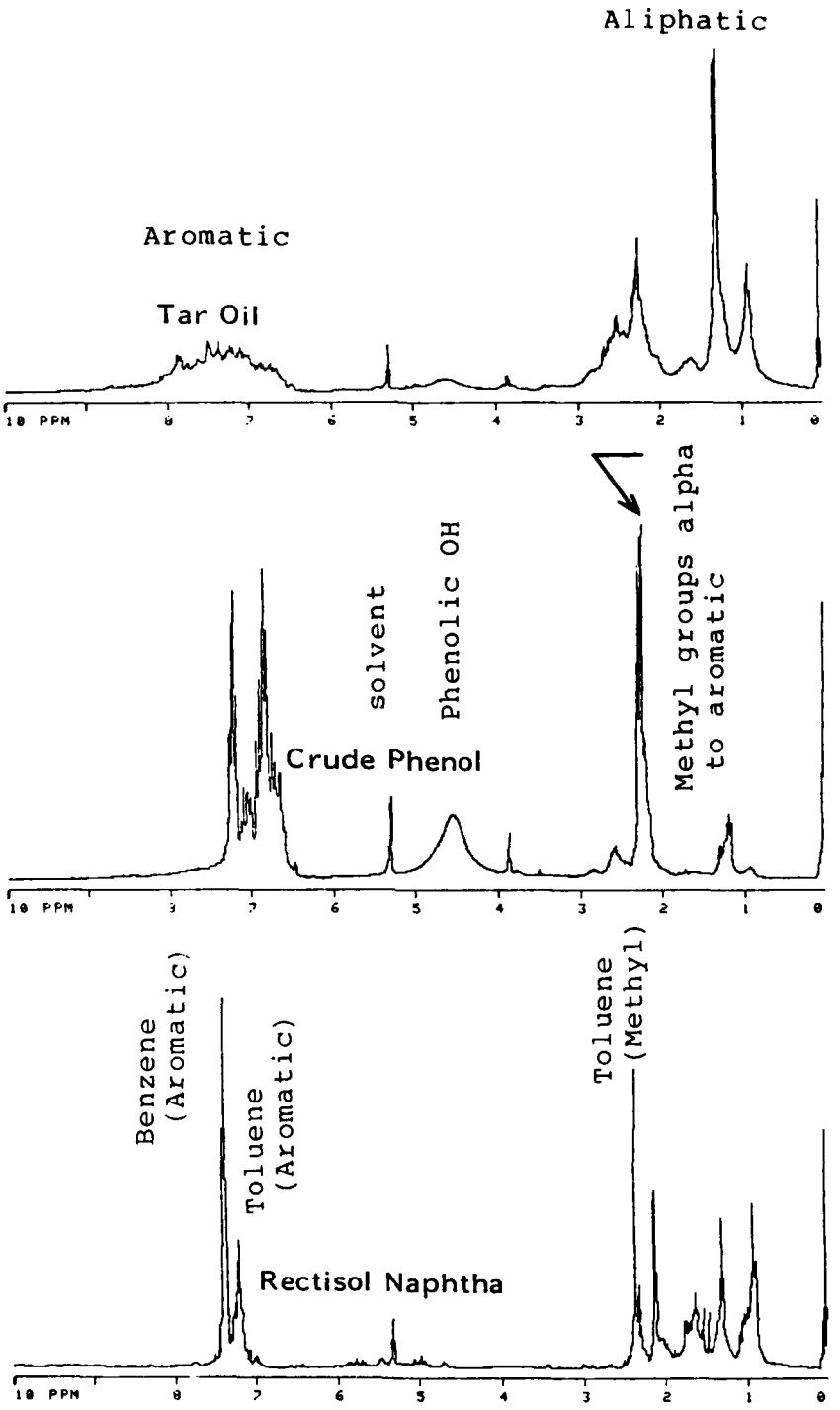


Figure 38. Proton NMR spectra of tar oil, crude phenol, and rectisol naphtha.

TABLE 36

PROTON AND CARBON-13 NMR DATA

Carbon Type	NMR Region ppm	AV Jet A %Area	Tar Oil %Area	Crude Phenol %Area	Rectisol Naphtha %Area
		PROTON NMR			
Aromatic	9.0 - 5.9	4.8	28.3	50.2	38.9
Phenol	4.4 - 3.5	0.4	2.4	16.9	0.4
Acenapthene	3.5 - 3.3	0.1	0.5	2.1	1.9
-CH2-alpha	3.3 - 1.9	6.5	28.4	23.5	22.2
-CH2-beta	1.9 - 1.5	7.8	5.3	1.3	10.5
-CH2-	1.5 - 1.0	43.6	23.4	4.8	13.9
-CH3	1.0 - 0.1	36.8	11.7	1.2	12.2
Total Area%		100.0	100.0	100.0	100.0
-CH2-/-CH3		1.2	2.0	4.0	1.1
		CARBON-13 NMR			
Aliphatic,C=	240-187	2.5		1.0	2.0
Aromatic,C=0	187-160	2.3		0.1	1.1
Phenolic	160-149	1.0		10.2	0.0
Aromatic,=C=	149-138	2.5		8.3	2.7
Aromatic,=C-	138-95	10.1		65.8	66.7
Methoxy	95-60	0.1		0.2	1.1
Aliph.,-CH2-	50-36	23.0		1.4	4.3
C	36-27	33.3		2.3	9.7
alpha C	27-17	16.8		5.2	8.0
-CH3	17-0	8.4		5.5	4.4
Total Area%		100.0		100.0	100.0

REFERENCES

1. Kleesattel, D.R., "Petrology of the Beulah-Zap Lignite Bed", UND Masters Thesis, 1985.

2. Kleesattel, D.R., "Petrographic Study of Beulah-Zap Lignite with Respect to Gasifier Performance", Final Report to ANG Coal Gasification Company, January 22, 1987.

LIST OF ABREVIATIONS

ANG	Associated Natural Gas
AR	as received
area%	area percent
ASTM	American Society for Testing Materials
AV Jet A	commercial aviation jet fuel type A
Bbl/D	barrels (42 gal) per day
B.P.	boiling point at one atmosphere
Btu	British thermal unit
BTX	mixture of benzene, toluene, and xylenes
^{o}C	degrees Celsius
CI	chemical ionization
EI	electron impact
ERC	Energy and Mineral Research Center
^{o}F	degrees Fahrenheit
FID	flame ionization detector
FTIR	fourier transform infrared
GC	gas chromatography
GC/FID	gas chromatography with a flame ionization detector
GC/MS	gas chromatography with a mass spectrometer
GPGP	Great Plains Gasification Plant
Hz	hertz
IBP	initial boiling point
JP-4	jet propulsion fuel, specification 4
JP-8	jet propulsion fuel, specification 8
K	kilo
^{o}K	degrees Kelvin
KGaus	kilogause
lb/hr	pounds per hour
KF-water	water content determined by Karl Fisher method
mf or MF	moisture free
ml or mL	milliters
ml/min	milliliters per minute
MM SCF	million standard cubic feet
MHz	megahertz
nm	nanometer
NMR	nuclear magnetic resonance
%	percent
ppm	part per million
Rf	Response factor
Ri	retention index
RAM	random access memory
ROM	read only memory
SNG	synthetic natural gas
Sp. Gr.	specific gravity
TBP	true boiling point
TCD	thermal conductivity detector
THFI	tetrahydrofuran insolubles (0.5 micron filter)
TI or TIC	total ion current in MS analysis
TMS	tetramethylsilane

LIST OF ABREVIATIONS (Cont.)

TPD	tons per day
uL	microliters
UNDEMRC	University of North Dakota Energy and Mineral Research Center
vol%	volume percent
vs.	versus
WRI	Western Research Institute
wt%	weight percent

U.S.Government Printing Office: 1988 548-054/80865